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CONTENTS.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

PAGE

I.—On the Constitution of Matter in the Gaseous State. By Ad. Wurtz, Membre de l'Institut; Doyen Honoraire de la Faculté de Médecine de Paris 1

II.—Comparison of the Actions of Hypochlorites and Hypobromites on some Nitrogen-Compounds. By H. J. H. Fenton, B.A., University Laboratory, Cambridge 12

III.—On the Action of Bromine upon Sulphur (Additional Note). By J. B. Hannay, F.R.S.E., F.C.S., lately Assistant-Lecturer on Chemistry in the Owens College, Manchester . 16

IV.—On the Determination of Lithia by Phosphate of Soda. By C. Rammelsberg 18

V.—On the Composition of Lithia-micas. By C. Rammelsberg. 19

VI.—Contributions from the Laboratory of the University of Tôkió, Japan:—(1.) On the Red Colouring Matter of the *Lithospermum erythrorhizon*. By M. Kuhara, Assistant in the Chemical Laboratory 22

VII.—Researches in Dyeing. Part I. Silk and Rosaniline. By Edmund J. Mills, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and George Thomson. 26

VIII.—Note on two New Vegeto-Alkaloïds. By Baron F. von Mueller and L. Rummel 31

IX.—A Chemical Study of Vegetable Albinism. By A. H. Church 33

X.—On a Hydride of Boron (Preliminary Notice). By Francis Jones, F.R.S.E. 41

XI.—On the Occurrence of certain Nitrogen Acids amongst the Products of Combustion of Coal-gas and Hydrogen Flames. By Lewis T. Wright 42

XII.—The Processes for Determining the Organic Purity of Potable Waters. By C. Meymott Tidy, M.B. 46

XIII.—Researches on the Action of the Copper-zinc Couple on Organic Bodies. Part IX. Preparation of Zinc-methyl. By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College 107

PAGE

XIV.—On Erbium and Yttrium. By J. S. Humpidge, B.Sc. (Lond.), Ph.D., and W. Burney 111

XV.—On the Formation of Barium Periodate. By S. Sugiura, Student in the Royal College of Chemistry, and C. F. Cross 118

XVI.—The Action of Alkaline Hypobromite on Oxamide, Urea, and Potassium Ferrocyanide. Part II. By William Foster, B.A., Lecturer on Chemistry, Middlesex Hospital Medical College 119

XVII.—The Derivatives of Di-isobutyl. By W. Carleton-Williams, Assistant Lecturer on Chemistry, The Owens College 125

XVIII.—On Stannic Ethide. By E. Frankland, F.R.S., and Awbrey Lawrance, Esq. 130

XIX.—On the Action of Isobutyric Anhydride on the Aromatic Aldehydes. By W. H. Perkin, F.R.S. 136

XX.—On Aurin (Part II). By R. S. Dale, B.A., and C. Schorlemmer, F.R.S. 148

XXI.—On Two New Methods for the Estimation of Minute Quantities of Carbon, (1) Gravimetric, (2) Chromometric, and their Application to Water Analysis. By A. Dupré, Ph.D., F.R.S., Lecturer on Chemistry at Westminster Hospital, and H. Wilson Hake, Ph.D., F.C.S. 159

XXII.—On the Action of Chlorine upon Iodine. By J. B. Hannay, F.R.S.E., F.C.S., Assistant Lecturer on Chemistry, Owens College, Manchester 169

XXIII.—Investigations into the Action of Substances in the Nascent and Occluded Conditions. Hydrogen (*continued.*) By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe 172

XXIV.—On Colouring Matters derived from Diazo-Compounds. By Otto N. Witt, Ph.D. 179

XXV.—On the Decomposition-Products of Quinine and the Allied Alkaloïds. By J. J. Dobbie, M.A., B.Sc., and W. Ramsay, Ph.D.—*Second Paper.* Oxidation of Quinine, Quinidine (Conquinine), Cinchonine, and Cinchonidine, with Permanganate 189

XXVI.—On the Action of Isomorphous Salts in Exciting the Crystallisation of Supersaturated Solutions of each other, and some Experiments on Supersaturated Solutions of Mixed Salts. By John M. Thomson, King's College, London 196

XXVII.—Quantitative Assay of the Ores and Compounds of Mercury by the Blowpipe. By George Attwood, F.G.S., Assoc. Inst. C.E., F.C.S., M. Am. Inst. M.E. 207

PAGE

XXVIII.—On some Points in the Analysis of Combustible Gases, and in the Construction of Apparatus. By J. W. Thomas 213

XXIX.—The Isomeric Dinaphthyls. By Watson Smith . . 224

XXX.—On the Occlusion of Hydrogen by Copper. By George Stillingfleet Johnson, Daniell Scholar of King's College, London 232

XXXI.—On Plumbic Tetrethide. By E. Frankland, F.R.S., and Awbrey Lawrance, Esq. 244

XXXII.—On the Decomposition of Water by Certain Metalloïds. By C. F. Cross and A. Higgin 249

Anniversary Meeting 257

XXXIII.—On Lead Tetrachloride. By W. W. Fisher, M.A., Aldrichian Demonstrator of Chemistry, Oxford . . . 282

XXXIV.—On Terpin and Terpinol. By William A. Tilden . 286

XXXV.—Researches in Dyeing. Part II. Note on the Emission of Colouring Matter. By Edmund J. Mills, D.Sc., F.R.S., and Louis Campbell 290

XXXVI.—On the Volumetric Determination of Chromium. By W. J. Sell, B.A., F.I.C., Demonstrator of Chemistry in the University of Cambridge 292

XXXVII.—On Heptane from *Pinus Sabiniana*. By T. E. Thorpe, Ph.D., F.R.S. 296

XXXVIII.—Preliminary Note on certain Compounds of Naphthalene and Benzene with Antimony Trichloride, &c. By Watson Smith 309

XXXIX.—Contributions from the Laboratory of Gonville and Caius College, Cambridge.—No. 1. On the Conditions affecting the Equilibrium of certain Chemical Systems.—No. 2. On the Action of Aqueous Hydrochloric Acid upon Bismuthous Chloride. By M. M. Pattison Muir, Caius Prælector in Chemistry 311

XL.—On the Action of Oxides on Salts. Part II. By Edmund J. Mills, D.Sc., F.R.S., and J. W. Pratt 336

XLI.—On the Determination of Tartaric Acid in Lees and Inferior Argol, with some Remarks on Filtration and Precipitation. By Beaumont J. Grosjean (J. B. Lawes's Chemical Works, Millwall, E.) 341

XLII.—On a New Class of Colouring Matters. By Otto N. Witt, Ph.D. 356

XLIII.—On a Method of Precipitating Manganese entirely as Dioxide, and its Application to the Volumetric Determination of Manganese. By John Pattinson, F.C.S., Newcastle-on-Tyne 365

PAGE

XLIV.—On the Determination of Nitric Acid as Nitric Oxide by means of its Action on Mercury. By ROBERT WARINGTON 375

XLV.—The Alkaloïds of the Aconites. Part IV. The Alkaloïds of Japanese Aconite Roots. By C. R. ALDER WRIGHT and A. P. LUFF (Appendix by C. R. ALDER WRIGHT and A. E. MENKE) 387

XLVI.—The Alkaloïds of the Veratrums. Part II. The Alkaloïds of *Veratrum album*. By C. R. ALDER WRIGHT, D.Sc. (Lond.), and A. P. LUFF 405

XLVII.—The Alkaloïds of the Veratrums. Part III. The Alkaloïds of *Veratrum viride*. By C. R. ALDER WRIGHT, D.Sc. (Lond.), Lecturer on Chemistry in St. Mary's Hospital Medical School 421

XLVIII.—On a Gold Nugget from South America. By GEO. ATTWOOD, F.G.S., Assoc. Inst. C.E., M.Am. Inst. M.E. . 427

XLIX.—On Nitrification. Part II. By ROBERT WARINGTON . 429

L.—Examination of Substances by the Time Method. Part I. Hydrates. By J. B. HANNAY, F.R.S.E., F.C.S. . . . 456

LI.—On the Volumes of Liquids at their Boiling Points, obtainable from Unit-volumes of their Gases. By WILLIAM RAMSAY, Ph.D., Tutorial Assistant of Chemistry in the University of Glasgow 463

LII.—Third Report to the Chemical Society on "Researches on some Points in Chemical Dynamics." Section I. By C. R. ALDER WRIGHT, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School, and A. P. LUFF. Sections II, III, and IV. By C. R. ALDER WRIGHT and E. H. RENNIE, M.A. (Sydney), Demonstrator of Chemistry in St. Mary's Hospital Medical School 475

LIII.—On Chlor-stannic Acid. By J. W. MALLET, F.R.S. . 524

LIV.—On the Action of Organo-Zinc Compounds on Quinones. (Preliminary Note.) By FRANCIS R. JAPP, M.A., Ph.D., Assistant in the Chemical Research Laboratory, Science Schools, South Kensington 526

LV.—On Indigo-purpurin and Indirubin. By EDWARD SCHUNCK, Ph.D., F.R.S. 528

LVI.—The Composition of Cows' Milk in Health and Disease. By A. WYNTER BLYTH 530

LVII.—Notes on the effect of Alcohol on Saliva, and on the Chemistry of Digestion. By WILLIAM H. WATSON, F.C.S. . 539

LVIII.—A Contribution to the Theory of Fractional Distillation. By T. E. THORPE, Ph.D., F.R.S. 544

LIX.—Theory of Fractional Distillation. By FREDERICK D. BROWN 547

PAGE

LX.—Transformation of Aurin into Trimethylpararosaniline. By R. S. Dale, B.A., and C. Schorlemmer, F.R.S. . . . 562

LXI.—On the Boiling Points of Certain Metals and Metallic Salts. By Thomas Carnelley, D.Sc., and W. Carleton Williams, Assistant Lecturers on Chemistry, Owens College 563

LXII.—On Dry Copper-zinc Couples and Analogous Agents. By J. H. Gladstone, F.R.S., Ph.D., and Alfred Tribe, Lecturer on Chemistry in Dulwich College 567

LXIII.—On the Determination of Nitric Acid by means of Indigo, with special reference to Water Analysis. By Robert Warington 578

LXIV.—Notes on the Purple of the Ancients. By Edward Schunck, Ph.D., F.R.S. 589

LXV.—Contributions to the History of Starch and its Transformations. By Horace T. Brown and John Heron . . 596

LXVI.—On the Action of Hydrochloric Acid on Manganese Dioxide. By Spencer Umfreville Pickering, Brackenbury Scholar of Balliol College, Oxford 654

LXVII. On the Decomposition of the Simple Weight χ effected by Victor Meyer. By Sir B. C. Brodie, Bart., F.R.S . 673

LXVIII.—Note on Safranine. By R. S. Dale, B.A., and C. Schorlemmer, F.R.S. 682

LXIX.—Suberic and Azelaïc Acids. By R. S. Dale, B.A., and C. Schorlemmer, F.R.S. 683

LXX.—On Gardenin. By J. Stenhouse, F.R.S., and Charles E. Groves 688

LXXI.—On the Heat of Formation of Aniline, Picoline, Toluidine, Lutidine, Pyridine, Dipicoline, Pyrrol, Glycerin, and Furfurol. By William Ramsay, Ph.D., Tutorial Assistant of Chemistry in the University of Glasgow 696

LXXII.—On the Atomic Weight of Tellurium. By W. L. Wills, B.Sc., Student in the Owens College Chemical Laboratories 704

LXXIII.—Note on the Magnesium Vanadates. By S. Sugiura and H. Baker, Students in the Chemical Laboratories of the Owens College, Manchester 715

LXXIV.—On Mauveine and Allied Colouring Matters. By W. H. Perkin, F.R.S. 717

LXXV.—On the Action of Sulphuric Acid on the Hydrocarbons of the Formula $C_{10}H_{16}$. By Henry E. Armstrong, PhD., F.R.S., and William A. Tilden, D.Sc. (London) . 733

LXXVI.—A Study of Certain Cases of Isomorphism. By Harry Baker, Dalton Chemical Scholar in the Owens College 760

PAGE

LXXVII.—On the Transformation-products of Starch. By C. O'Sullivan 770

LXXVIII.—On a New Method of Determining Sulphur in Coal. By Teikichi Nakamura, Student of the Imperial College of Engineering (Kobudaigakko), Tôkiô, Japan 785

LXXIX.—The Bromine Derivatives of β-Naphthol. By Alfred J. Smith, B.Sc. 789

LXXX.—The Action of Phosgene on Ammonia. By H. J. H. Fenton, B.A., University Laboratory, Cambridge . . 793

LXXXI.—Rehydration of Metallic Oxides. By Charles F. Cross 796

LXXXII.—Alizarin-blue. By G. Auerbach 799

LXXXIII.—On Ethylene Chlorothiocyanate and its Oxidation into Chlorethylsulphonic Acid. By J. William James . 806

LXXXIV.—Notes on the Dissociation of Ammonia Iron Alum. By John S. Thomson 811

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THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*On the Constitution of Matter in the Gaseous State.*

By Ad. Wurtz, Membre de l'Institut; Doyen Ordinaire de la Faculté de Médecine de Paris.

[The Faraday Lecture, delivered before the Fellows of the Chemical Society, in the Theatre of the Royal Institution, on Tuesday, November 12, 1878.]

Ladies and Gentlemen,—I esteem it a great honour to address you within these walls, about which there still hovers the ever fresh memory of him whose name we celebrate to-day, while we deplore his loss. I am fully sensible both of the great value of this honour, and of the danger that attends it, and I have need to shelter myself under the authority of the great name of Faraday. I have, therefore, chosen a subject connected with his earliest discoveries. The constitution of matter is a question of the highest importance with regard both to physics and to chemistry.

The word *gas* was introduced into science by Van Helmont, who, at the beginning of the 17th century, first pointed out, with some degree of precision, the differences existing between certain aëriform fluids. He it was who first spoke of *Gas sylvestre*, formed by the combustion of charcoal, and given off during the fermentation of beer. To him also we owe the distinction—which kept its ground for two centuries—between gases and vapours. He regarded gases as aëriform fluids incapable of reduction to the liquid state by cooling, whereas vapours require the aid of heat to maintain them in the gaseous state. An important difference of constitution seemed, therefore, to exist between these two kinds of aëriform fluid. This difference, however, is not fundamental, and the distinction between gases and vapours has disappeared, in a theoretical point of view, being in fact reduced to a simple question of temperature and pressure.

On March 23, 1823, Faraday, then a young man engaged as chemical assistant at the Royal Institution, read before the Royal Society a note entitled "On Fluid Chlorine." He had succeeded in condensing this gas to a liquid by a process which has become classical. This process consists in heating in a closed vessel placed in a water-bath crystals of chlorine hydrate. This compound, very rich in chlorine, is resolved at a gentle heat into chlorine and liquid water, the quantity of which is not sufficient to dissolve the whole of the chlorine. The latter is therefore disengaged in great part in the state of gas, which accumulates in the small space remaining to it, and is liquefied by the pressure which it exerts upon itself.

On the same day Sir Humphry Davy read a note "On the Liquefaction of Hydrochloric Acid Gas," which he effected by decomposing sal-ammoniac with sulphuric acid in a closed vessel. These researches were completed by Faraday, who, on April 10 of the same year, described the liquefaction of a large number of gases, directing his efforts, by Davy's advice, chiefly to those which are dense, or very soluble in water, such as sulphurous acid, ammonia, sulphuretted hydrogen, carbonic acid, and protoxide of nitrogen.

To enumerate the special processes adopted in each particular case would occupy too much time. We shall therefore merely observe that the chief, if not the only, means of condensation adopted in these experiments was compression, that is to say, the reduction of the gas to a small volume, and that this compression was exerted by the gas upon itself, as it accumulated in the very strong sealed glass tubes in which it was disengaged. Sir Humphry Davy, in the note above cited, had remarked that pressure appeared to be a more efficacious method of condensation than cooling, inasmuch as a double pressure reduces the volume of the gas to one-half, whereas a depression of temperature of 1° F. reduces the volume by only $\frac{1}{480}$, the lowering of temperature, moreover, soon attaining an impassable limit. It must, however, be especially observed that Faraday, evenin his first experiments, made use of differences of temperature, if not to liquefy the gases, at all events to distil and isolate the liquids. Thus it was in the case of chlorine, for example, and in that of ammonia, which he liquefied by heating ammoniacal silver chloride in a bent tube sealed at both ends, the liquid ammonia then distilling over and collecting in the empty branch of the tube, which was cooled to a low temperature.

Similar phenomena will be exhibited in the experiment which I am about to show you, consisting in the liquefaction of cyanogen gas, by heating cyanide of mercury in a small glass tube terminated by a long capillary tube bent in the form of the letter U. The figure of this curved portion will be projected on a screen by the electric light,

and in a few seconds you will see the liquid cyanogen collect in the bend.

Before leaving this part of my subject, I would recall to your attention two of Faraday's discoveries, resulting from the application of the principles just explained. Having compressed coal-gas to 25 atmospheres, Faraday, in 1825, discovered two important bodies, namely, *butylene*, a compound of great importance in a theoretical point of view, and *benzene*,—so named by Mitscherlich several years afterwards,—which in our own time has become the object of numerous and important applications, and the pivot of an entire department of chemistry.

Another instance is afforded by sulphurous acid gas (SO_2), which was liquefied by Bussy in 1824, at the ordinary atmospheric pressure, by the effect of a cold of 12° to 15° below zero.

Whether we condense gases by pressure, or reduce them to the liquid state by diminution of temperature, the result of either method is to bring their particles closer together. It would seem then, in accordance with Davy's view, that pressure ought to be more efficacious, as a means of condensation, than cooling. Nevertheless it is not so. The mere approximation of the particles of certain gases does not suffice to effect their liquefaction, and, moreover, the distances between the particles cannot be diminished indefinitely by pressure alone. M. Natterer, of Vienna, has compressed oxygen, hydrogen, and nitrogen to 3000 atmospheres, without effecting their liquefaction. These gases, hitherto called permanent, cannot be liquefied by pressure alone, and their liquefaction, which has quite recently been effected, is the joint effect of strong pressure and a great degree of cold. This is the important point, and I request your permission to offer in this place a few explanations which will serve to place it in its true light.

The impossibility of liquefying certain gases by pressure alone is in accordance with the ideas which are current at the present day respecting the nature of aëriform fluids, and likewise with a discovery made in England within the last few years, on the continuity of the gaseous and liquid states. I will explain myself briefly on these two points.

Daniel Bernoulli first enunciated the idea that gases are formed of material particles, free in space, and animated by very rapid rectilinear movements, and that the tension of elastic fluids results from the shock of their particles against the sides of the containing vessels. Such is the origin of the kinetic theory of gases, which has been revived since 1824 by Herapath, Joule, and Krönig, and developed chiefly by Clausius and Clerk-Maxwell.

The law of Boyle and of Mariotte follows as a natural consequence of this idea. Suppose a gas occupying a certain volume, and

composed of a definite number of material particles—or molecules so called—to be contained in a closed vessel, such as the cylinder of an air-pump; the pressure on the piston will be determined by the number of shocks of the molecules diffused through the neighbouring stratum of gas. If, then, the volume of the gas be reduced, the number of particles in this layer will be increased, as well as the sum of the shocks, and the pressure will be increased in proportion thereto.

The velocities with which these molecules move are enormous. Clausius supposes that the molecules of air move with a mean velocity of 485 metres per second, and those of hydrogen with a mean velocity of 1844 metres per second. I say mean velocity, for all the particles of a gas do not move at the same rate. But can the particles freely traverse these wide spaces? By no means; their number is so immense that every instant they enter into collision with one another, and rebound in such a manner that their motion is altered both in velocity and in direction. It follows, therefore, that the molecules of a gaseous mass are continually moving in all directions with variable velocities, their motion in the intervals between the collisions being sensibly rectilinear. The distribution of the velocities has been made the subject of important researches by Clerk-Maxwell.

These movements of gaseous molecules determine a very important physical condition, namely, *temperature*. In fact, the energy of the rectilinear movements, that is to say, the masses of the gaseous molecules multiplied by the square of the velocity, gives the measure of the temperature, which consequently increases proportionally to the energy of the rectilinear movement, or, for the same gas—since the masses remain constant—it increases as the square of the velocity. If the velocity were reduced to nothing, the calorific motion would be annihilated, that is to say, the gas would be entirely deprived of heat. This state corresponds with the absolute zero.

The gaseous molecules moving in all directions, and coming into collision with one another in space, are very nearly emancipated from cohesion. Nevertheless this attractive force makes itself felt for the infinitely short time during which the molecules actually touch one another, or are on the point of doing so. This influence of cohesion is one of the causes of deviation from the law of Boyle or of Mariotte.

In liquids the influence of cohesion is manifest, preventing the molecules from separating, though it allows them to glide one over the other. This molecular cohesion, or attraction, is in continual strife with the force of expansion, or kinetic energy, which, if unopposed, would launch the molecules into space.

To understand the antagonism between these two forces, consider for a moment a saturated vapour in contact with the liquid from which it has been formed. When it is reduced to a smaller volume, a certain

number of its molecules are brought within the sphere of action of cohesion; they are consequently aggregated together and precipitated in the liquid state, while the rest, being now diffused through a wider space, continue to move with the same velocity, and to exert the same pressure as before. In this case the force of cohesion of the liquid particles exactly balances the expansive force or kinetic energy, and serves to a certain extent as a measure of its amount.

Now let the vapour be heated, after it has been withdrawn from the action of the liquid; its expansive force will then increase; it will dilate, and may then be compressed, until, by the approximation of its particles, it is again brought within the sphere of action of the cohesive force,—that is to say, to the point of saturation corresponding with the temperature to which it has been raised. With the increase of temperature, the expansive force or kinetic energy of the vapour likewise increases, whereas the cohesion of the liquid becomes less: hence the necessity of further diminishing the distances between the particles by increase of pressure. But this double effect of increased kinetic energy of the gaseous molecules, and diminished cohesion of the liquid molecules, going on progressively as the temperature rises, a point will at length be attained at which the energy of the molecular movement will finally gain the victory over the force of cohesion, *whatever be the pressure to which the vapour is subjected.* The minimum temperature at which this effect is produced, and at which, therefore, a vapour can no longer co-exist with its liquid under any pressure whatever, has been called, by my friend Dr. Andrews, the *critical point*, and by M. Mendelejeff the absolute *boiling-point.* Above this temperature, whatever may be the pressure, the gas, whether dilated or compressed, will maintain the same physical state, characterised by freedom of molecular or calorific movement.

I can show you by experiment this peculiar phenomenon of the sudden passage of a liquid mass to the state of gas, by heating liquid carbonic acid in a closed vessel, just as Cagniard de Latour formerly heated ether. Here is a tube, half filled with liquid carbonic acid, which we are about to immerse in water at 35°: you observe that the liquid first rises quickly in the tube, its coefficient of expansion being greater than that of gases; at the same time the meniscus flattens more and more, indicating a diminution of cohesion in the liquid (Andrews), and finally disappears altogether; in fact the liquid itself has disappeared, having been entirely and suddenly transformed into gas. What now must we do to cause it to reappear? We must lower the temperature, so as to diminish the kinetic energy of the gas, and increase the cohesion of the liquid. A moment will then arrive when the cohesive force will again be able to resume the contest, and the liquid will be reconstituted.

We are now in a position to understand why certain gases, hitherto called *permanent*, cannot be liquefied, except by the combined action of very strong pressure and a very great degree of cold. The critical points of these gases are situated at very low temperatures. They have quite recently been liquefied, this great discovery having been made by MM. Cailletet and Raoul Pictet.

The principle of Cailletet's apparatus is the following:—The gas to be liquefied is introduced into a cylindrical glass vessel, and transferred by means of mercury to a very strong glass tube sealed into the reservoir. This latter is firmly fixed in a cylindrical cavity hollowed out of a block of iron, and serving as a kind of closed mercurial trough. The cylindrical cavity communicates with a hydraulic press which injects water on to the surface of the mercury, driving it into the gas reservoir, which is ultimately quite filled with that liquid, the gas being thereby driven into the tube, where it is liquefied.

In this manner we shall be able by a few strokes of the piston of the hydraulic press to liquefy carbonic acid. Other gases less easily condensable may be liquefied in a similar manner, if the tube be cooled to $-20°$ or $-30°$. But these temperatures do not suffice for the liquefaction of the so-called permanent gases. To cool these gases to lower temperatures, M. Cailletet avails himself of sudden expansion (*détente*). The gas, compressed to several hundreds of atmospheres, when allowed to expand suddenly, and drive the air before it, consumes a certain quantity of heat, and is thereby reduced to a kind of mist, which will appear on the screen, and pass away like a cloud, if we suddenly expand the strongly compressed carbonic acid gas, which we have here, in default of oxygen or hydrogen.

M. Raoul Pictet has succeeded in condensing oxygen and hydrogen in the form of liquids, properly so called, and even in obtaining the latter of these gases in the solid state. To produce this effect, he employs condensing apparatus of incomparable power, combining the action of a cold of 120—140° below zero with that of enormous pressures amounting to 550 and even 650 atmospheres. The pressure is produced by the accumulation of the gases in a closed space consisting of a long copper tube of very thick metal. The oxygen was produced by heating potassium chlorate in a howitzer shell, having a copper tube soldered into its orifice. The hydrogen was prepared in a similar apparatus, by decomposition of a dry mixture of potassium formate and potassium hydroxide.

To produce very low temperatures of 120° or even 140° below zero, M. Pictet resorts to a very ingenious artifice. Over the reservoir-tube which surrounds the copper tube, and in which these low temperatures are intended to be produced, he superposes another system

of concentric tubes, intended to produce a first fall of temperature amounting to —65°, by the volatilisation of liquid sulphurous acid. By means of this first depression of temperature it has been found possible to liquefy carbonic acid gas in the inner tube of the system just mentioned, by a pressure of only a few atmospheres. The carbonic acid thus liquefied being introduced into the lower reservoir-tube of the apparatus, produces by its volatilisation a second fall of temperature round the copper tube containing the compressed oxygen which is to be liquefied. M. Pictet has in fact established a double circulation, one of sulphurous acid, the other of carbonic acid. I will describe the former. Sulphurous acid gas is liquefied by a pressure of three atmospheres, and collects in a strong vessel, from which it passes through a tube into the upper reservoir. The pressure is exerted by means of a force-pump. A suction-pump connected with the force-pump, and acting in concert with it, withdraws the liquid sulphurous acid from the reservoir-tube, and transfers it to the force-pump, which brings it back to the vessel, and thence to the upper reservoir-tube.

The circulation of the carbonic acid is established in the same manner, by means of two pumps, one of which condenses the gas by forcing it into tubes cooled to — 61°, while the other, which is a suction-pump, sends it back to the force-pump. The volatilisation of the carbonic acid produces round the copper tube the low temperatures above mentioned. The copper tube is, in fact, surrounded by solid carbonic acid.

In this manner M. Pictet has liquefied oxygen, and has approximately calculated its density. He has also liquefied and even solidified hydrogen, which he has seen to issue from the tube in the form of a steel-blue liquid jet, which partly solidified. The solid hydrogen, in falling on the floor, produced the shrill noise of metallic hail, thus confirming the bold and ingenious idea, first suggested by Faraday, that hydrogen is a metal.

The experiments of MM. Raoul Pictet and Cailletet have, then, removed from science the distinction between permanent and condensable gases. Permanent gases exist no longer. All aëriform fluids may be liquefied with a facility greater in proportion as their critical points are situated at higher temperatures. From a physical point of view, therefore, gases and vapours have the same constitution, being formed of molecules which move freely in space. In what, then, do they differ? They differ by the nature and constitution of these molecules; and here we enter on the domain of chemistry.

It is supposed in chemistry that the molecules of each species of gas or vapour are formed of a definite number of atoms. The simplest molecules, like those of mercury vapour, are formed of single atoms. Others include several atoms of the same or of different kinds; and

these latter molecules may be very complex, that is to say, formed of a large number of atoms held together by affinity, and vibrating in concert in a system to which they are attached, viz., the molecule. In this system, which has a definite form, extent, and centre of gravity, the molecules execute their own proper movements, and are at the same time carried forward with the entire system in the molecular paths.

I cannot here dilate on the nature and chemical properties of the several gases and vapours. I wish merely to throw light on a single point, which is of great importance, inasmuch as it constitutes one of the fundamental conceptions of chemical science.

The proposition which I am about to enunciate is generally adopted by chemists, resting as it does on an imposing array of facts:—*Equal volumes of gases or vapours, under the same conditions of pressure and temperature, contain equal numbers of molecules.*

The Italian chemist, Amadeo Avogadro, in discussing the discoveries of Gay-Lussac respecting the simple relations which exist between the volumes in which gases combine, was the first to recognise that there likewise exists a simple relation between the volumes of gases and the number of molecules which they contain. The simplest hypothesis, said he, that can be made regarding this matter, consists in supposing that all gases contain in equal volumes equal numbers of "integrant molecules." By this term he denoted what we now call simply *molecules*, and he distinguished these integrant molecules from the "elementary molecules," which we call *atoms*. According to him, the integrant molecules of gases are all equally distant one from the other, and these distances are so great in proportion to the dimensions of the molecules, that the mutual attraction between the latter is reduced to nothing.

These integrant molecules are composed of a greater or smaller number of elementary molecules, not only in compounds, but likewise in simple bodies; the integrant molecules of chlorine, for example, are composed of four elementary molecules, and the same is the case with the integrant molecules of hydrogen. What happens, then, when chlorine and hydrogen combine together? The integrant molecules of these two bodies are then resolved into elementary molecules, which combine, two by two, to form hydrochloric acid.

Ideas analogous to those of the Italian chemist were enunciated in 1814 by Ampère, and thus there has been introduced into chemical science the notion that there exist two kinds of small particles, namely, molecules and atoms, the former being diffused in equal numbers through equal volumes of gases.

But this notion, so clearly enunciated more than 60 years ago, was afterwards destined to be obscured. Berzelius, taking up Ampère's

proposition, altered it by substituting atoms for molecules, and saying that "equal volumes of gases contain equal numbers of atoms." This proposition, which has given rise to long discussions, must now be rejected, for it is inexact. It is to Gerhardt, and more recently to Cannizzaro, that is due the honour of having restored the proposition of Avogadro and Ampère, in its original form, and pointed out its importance in connection with chemical theory. This I must explain in conclusion.

In the first place Gerhardt simplified the rule of Avogadro. The latter supposed that a molecule of chlorine or of hydrogen contains four atoms, whereas Gerhardt regards it as consisting of two. Avogadro's proposition thus modified, assumes a very simple form, and may be enunciated in the following terms:—Suppose that a volume, or the unit of volume, of hydrogen contains one atom: then the molecules of all gases and vapours will occupy two volumes. Thus, a molecule of hydrogen formed of two atoms will occupy two volumes, and a molecule of chlorine formed of two atoms will likewise occupy two volumes. What, now, will happen when chlorine combines with hydrogen? The molecules will be cut in two, and each of the two chlorine atoms, uniting itself to an atom of hydrogen, two molecules of hydrochloric acid will be formed, each occupying two volumes. Thus, if an atom of hydrogen occupies one volume, a molecule of hydrochloric acid will occupy two volumes. The same is the case with the molecules of all other gases and vapours:—

1 mol.	water	formed of	2 at. H and 1 at. O	occupies 2 vols.
„	ammonia	„	3 at. H and 1 at. N	„ „
„	marsh-gas	„	4 at. H and 1 at. C	„ „

This list might be prolonged by taking as examples a large number of gaseous or volatile bodies belonging both to mineral and to organic chemistry, and including chlorinated, brominated, and oxygenated compounds of the metalloïds, and of a large number of metals. The countless volatile compounds of organic chemistry, hydrocarbons, alcohols, chlorides, bromides, organo-metallic compounds, compound ammonias, aldehydes, ketones—all this legion of divers compounds—conform to the law of Avogadro and Ampère, their molecules occupying two volumes if an atom of hydrogen occupies one volume. Hence it follows that the relative weights of two volumes represent the relative weights of the molecules or the molecular weights. To find these latter, therefore, it is sufficient to double the numbers which express the weights of a single volume, or of the unit of volume, that is to say the densities. The densities of gases may be referred to that of hydrogen as unity, and the atomic weights also to that of hydrogen. The unit being then the same, it follows that the numbers which express

the double densities referred to hydrogen will also represent the molecular weights.

Chemists represent the constitution of molecules by formulæ, each of which shows the number of atoms condensed within the molecule. Now the molecular weights being known, it is very easy to deduce the formulæ from them, as these formulæ must represent the number of atoms comprised in two volumes. Such is the relation which exists between the law of volumes and chemical notation. The rule of Avogadro and Ampère has, in fact, become one of the bases of this notation. There are, however, certain exceptions to its generality, but they are probably more apparent than real. Sal-ammoniac, ammonium sulphydrate, phosphorus pentachloride, iodine trichloride, sulphuric acid, calomel, amylene hydrobromide, and chloral hydrate, have vapour-densities such that their molecules appear to occupy four volumes. Such, however, is not the case; and it may be shown that the bodies in question do not volatilise without decomposition, but that, when they are heated, their molecules split up into two, each of which occupies two volumes. Being unable to analyse all these cases above-mentioned, I will confine myself to the last, viz., chloral hydrate, which has given rise to a long discussion.

The question to be decided is, whether this compound is or is not decomposed by conversion into vapour. If it really suffers decomposition, it should be resolved into anhydrous chloral and water. That this decomposition takes place may be shown by a method based on the theory of dissociation developed by M. H. Ste.-Claire Deville.

Here is the case in a few words. We have here in a tube a certain volume of the vapour of chloral hydrate under a certain pressure; it is required to show that this vapour contains vapour of water. For this purpose we are about to introduce into it a body capable of emitting vapour of water, crystallised potassium oxalate for example. If the atmosphere is dry, this salt will give off vapour of water just as it would in dry air or in vapour of chloroform at the same temperature, and it will continue to emit this vapour until the atmosphere shall have taken up a degree of humidity corresponding with that which is designated by M. H. Ste.-Claire Deville as the *dissociation tension* of the hydrated salt in question. If, on the other hand, the chloral atmosphere is moist, and exhibits exactly the degree of humidity just defined, the crystallised oxalate will not emit any water. In this first tube, then, we have the vapour of chloral hydrate; the second contains vapour of chloroform. This latter is dry, and I am about to prove to you that the former is moist. In fact, the crystallised potassium oxalate which we are introducing into the chloroform tube will rapidly depress the level of the mercury

by emitting vapour of water, whereas in the atmosphere of chloral hydrate it will not emit vapour of water, and consequently will not depress the level of the mercury. This shows that chloral hydrate undergoes decomposition when converted into vapour, and this supposed exception to the rule of Avogadro and Ampère vanishes, like all the rest, when submitted to the test of experiment. This rule appears, then, like a grand law of nature, as simple in its enunciation as it is important in its consequences.

Such are the considerations which I wished to lay before you on the physical and chemical constitution of the gases. Does not this exposition seem to show that, of all the states which matter can assume, the gaseous state is the most accessible to our researches, and the best known—not, indeed, that we can affirm the certainty of the theoretical considerations which I have brought before you, for they are but probable. In the physical sciences nothing is certain but well observed facts and their immediate consequences; and, whenever we attempt to make these facts the basis of any general theory, hypothetical data are apt to mix themselves up with our deductions. In the present case the hypothesis consists in assuming that gases, and matter in general, are formed of molecules, and these latter of atoms. No one has ever seen these molecules and atoms, and it is certain that nobody will ever see them. Does it follow, then, that we ought to reject or disdain this hypothesis? By no means. Our theories may be verified in their consequences, and may thereby acquire a certain degree of probability. The theory under consideration has been subjected to this ordeal, and nothing has hitherto been found to contradict it. Yes, it is probable that gases are composed of small particles moving freely in space, with immense velocities, and capable of communicating their motion by collision or by friction. It is probable that these molecules are diffused in space in numbers so enormous that the most rarefied spaces still contain legions of them; and it is this circumstance which explains the possibility of the movements of the radiometer.

Be this as it may, the idea of Daniel Bernouilli has been developed into a beautiful theory—the kinetic theory of gases—a theory which has shed a sudden clearness, an unexpected light, on matters which seemed to be veiled in the deepest obscurity. The molecules, as already stated, are invisible. Nevertheless, attempts have been made to penetrate this invisible world by the force of scientific reasoning, and by an effort which does honour to the human mind, even if it be destined to remain barren. The illustrious authors of the kinetic theory of gases have sought to determine, not only the velocities of the gaseous molecules, and the prodigious number of their collisions during a unit of time, but likewise their distances, their absolute dimensions, and their number in a given volume. And here we arrive at results

which bewilder the imagination, but which, in this lecture, I must not attempt to unfold.

Permit me only to add that these great labours mark a resting-place in our course, and are, perhaps, an approach towards the solution of the eternal problem of the constitution of matter—a problem which dates from the earliest ages of civilisation, and though discussed by all the great thinkers of ancient, as well as of modern times, still remains unsolved. May we not hope that in our own time this problem has been more clearly stated and more earnestly attacked, and that the labours of the 19th century have advanced the human mind in these arduous paths, more than those of a Lucretius, or even of a Descartes and a Newton. From this point of view, the discoveries of modern chemistry, so well expressed and summarised by the immortal conception of Dalton, will mark an epoch in the progress of the human mind; and to one of the most important among these discoveries —that of the liquefaction of the gases—grateful posterity will for ever join the glorious name of Faraday.

II.—*Comparison of the Actions of Hypochlorites and Hypobromites on some Nitrogen-Compounds.*

By H. J. H. Fenton, B.A., University Laboratory, Cambridge.

In a former paper (*Chem. Soc. Jour.*, July, 1878) I showed that urea, when acted upon by a hypochlorite in presence of a caustic alkali, gives off only one-half of its nitrogen in the cold, the other half remaining probably as a cyanate, whereas a hypobromite, as is well known, causes all the nitrogen to be evolved.

I thought, therefore, that it would be of interest to compare the actions of these two reagents on some bodies more or less analogous to urea in constitution.

The first substance I selected for experiment was *carbamate of ammonium*, the interesting results of Kolbe and Basaroff (*Chem. Soc. Jour.* [2], **6**, 194) having shown the close relation of this body to urea. The sample used was prepared by union of the dry gases. Weighed quantities of it having been enclosed in thin stoppered tubes, were introduced into flasks containing the hypochlorite or hypobromite solution, and excess of caustic alkali. The flasks having been connected with delivery-tubes, the thin vessels containing the ammonium carbamate were broken by shaking, and the resulting gas measured, in the same manner as in my experiments on urea.

When either hypochlorite or hypobromite of soda is used, a rapid

evolution of nitrogen ensues, but, as in the case of urea, only half the nitrogen is given off with the hypochlorite, and the whole with hypobromite.

Thus, with hypochlorite of soda—

(1.) ·1063 gram ammonium carbamate gave 15·5 c.c. N., and
(2.) ·1293 „ „ „ 19·49 c.c.

theory requiring (for the whole of the nitrogen) 30·52 c.c. and 37·1 c.c. respectively.

With hypobromite of soda

·0610 gram gave ..... 17·29 c.c. N
Theory requiring ..... 17·50 „

The residue from the action of hypochlorite of soda, as is the case with urea, shows no ammonia reaction with Nessler's solution, and gives off no more gas, even with a large excess of hypochlorite (except on long standing, when a slow decomposition appears to take place); but if, after reducing the excess of hypochlorite with SO_2, the solution be acidified with hydrochloric acid, abundant ammonia reactions are obtained.

The residue from the action of a hypochlorite on urea, however, was shown to be unaffected by the addition of a hypobromite, whereas, if this carbamate residue be so treated, a rapid evolution of the remaining half of the nitrogen takes place.

Thus, the residue from experiment (1) above, treated with hypobromite of soda, gave 14·7 c.c. N., and that from (2) gave 18·21 c.c.

It is evident, therefore, that the remaining half of the nitrogen in the carbamate residue does not exist as a cyanate. Moreover, if to this residue a slight excess of ammonia be added, and then a slight excess of calcium chloride, and the solution be filtered, the clear filtrate gives on boiling an abundant precipitate of calcium carbonate.

I conclude, therefore, that the nitrogen remains in this residue, in the form of carbamate of soda. Thus:—

$$2NaClO + 2(CONH_2.ONH_4) = 2NaCl + 2(CONH_2.ONa) + N_2 + 4H_2O.$$

A solution possessed of exactly similar properties as this residue is obtained by dissolving carbamate of ammonium, or the commercial carbonate, in strong caustic soda, and allowing the mixture to stand over sulphuric acid for a day or two.

It appears, therefore, that carbamate of soda can exist, and is tolerably stable in presence of caustic soda.

The action of hypobromite of soda thus affords a ready method of distinguishing a carbamate from a cyanate.

The next substance which engaged my attention was *guanidine*, Wanklyn and Gamgee and others having suggested its relation to urea, both possibly being derivatives of marsh-gas (*Journ. Chem. Soc.* [2], **6**, 31).

Urea.

Guanidine.

Crystals of guanidine carbonate and nitrate were used, and the experiments conducted in the same way as before.

·1925 gram of guanidine carbonate gave 43·7 c.c. N with sodic hypochlorite. Theory = 71·8 c.c.; and

·2523 gram gave 64·16 c.c. N with hypobromite. Theory = 94·1 c.c.

Again, ·1664 gram of guanidine nitrate gave 32·18 c.c. N with hypochlorite. Theory = 45·7; and

·1136 gram gave 20·24 c.c. with hypobromite. Theory = 31·25.

It appears, therefore, that the yield of nitrogen is approximately the same with either reagent, and that this is equivalent to almost exactly two-thirds of the total nitrogen, one-third remaining behind in either case, probably as a cyanate: for the residues from these reactions behave just like that from the action of hypochlorites on urea, giving no ammonia reactions until acidified.

The evolution of nitrogen is almost equally rapid with either reagent in this case.

Biuret was next tried in a similar way.

		Theory.
·1935 gram with hypochlorite	gave 21·38 c.c. N	= 63·06
·1322 „ hypobromite	„ 27·43 c.c. N	= 43·09

These numbers correspond with an evolution of almost exactly one-third of the total nitrogen with a hypochlorite, and of two-thirds with a hypobromite.

The residues from these reactions appear to behave like that from urea, the hypochlorite residue being unaffected by the addition of a hypobromite, and giving no ammonia reaction until acidified.

In the case of hypochlorite, the evolution of nitrogen is here slow, whereas with hypobromite it is immediate, as is the case with urea.

The quantities of nitrogen evolved by these two reagents from those bodies which I have as yet investigated, are therefore as follows:—

	Urea.	Ammonium carbamate.	Guanidine.	Biuret.	Ammonia salts.	Cyanates.
NaClO....	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	all	none
NaBrO....	all	all	$\frac{2}{3}$	$\frac{2}{3}$	all	none

The nitrogen in these bodies evidently exists in three distinct conditions as regards the action of these two reagents. 1st, that which is evolved by either hypochlorite or hypobromite; 2nd, that which is evolved by hypobromite only; 3rd, that which is evolved by neither reagent.

When hypochlorite of soda acts upon *urea* or *biuret*, the nitrogen originally existing in the second condition is transformed into the third condition.

It may be noticed that in these two reactions the evolution is slow, whereas in the others, the effect produced is almost instantaneous.

It is not easy to reconcile these facts with the formulæ usually adopted for the above compounds.

The formula for urea, however, proposed by Wanklyn and Gamgee $C\begin{smallmatrix}OH\\=NH\\NH_2\end{smallmatrix}$, or that suggested by Heintz (*Ann. Chem. Pharm.*, **150**, 73) and others, $C\begin{smallmatrix}\|O\\\end{smallmatrix}\!\!=\!\!N\!-\!\!\begin{smallmatrix}H\\|\\H\end{smallmatrix}\!\!-\!\!N\begin{smallmatrix}H\\|\\H\end{smallmatrix}$, will readily explain the actions of the two reagents on this body.

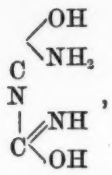
We might, for instance, assume that the *first* condition of nitrogen mentioned above is that in which it is united to carbon by one of its "affinities;" the *second* by two; and the *third* by three.

Now taking Wanklyn's formula, it is evident that a hypochlorite would remove the NH_2 group, leaving $\begin{smallmatrix}C\\|\end{smallmatrix}\!\!\begin{smallmatrix}OH\\=NH\end{smallmatrix}$, and this being incapable of existence, would lose H and become $C\begin{smallmatrix}OH\\\equiv N\end{smallmatrix}$, or normal cyanic acid. The nitrogen being now in the third condition, is no longer capable of being attacked by a hypobromite or hypochlorite.

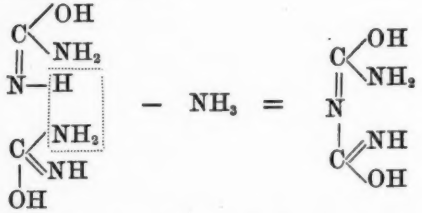
Ammonium carbamate may be $C\begin{smallmatrix}OH\\=NH\\ONH_4\end{smallmatrix}$, and this, when acted upon by a hypochlorite, loses NH_3, and (in presence of caustic soda) $C\begin{smallmatrix}OH\\=NH\\ONa\end{smallmatrix}$ remains. The nitrogen in this body being in the second condition, is attacked only by hypobromite.

In *biuret* we have three atoms of nitrogen, each in a different condition.

Its constitution may therefore be—

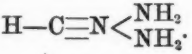


being formed from urea thus :—



In *guanidine* there are two atoms of nitrogen in the first condition, both being evolved by a hypochlorite or hypobromite, and one in the third condition being unattacked by either.

Its constitution, on the above supposition, must therefore be represented in some such way as—



III.—*On the Action of Bromine upon Sulphur (additional Note).*

By J. B. Hannay, F.R.S.E., F.C.S., lately Assistant-Lecturer on Chemistry in the Owens College, Manchester.

In former papers (*Chem. Soc. Journ.*, 1873, p. 823, and 1878, p. 284) it was shown that when sulphur and bromine were distilled together, distillates of any desired composition might be obtained, but that the residue could never be obtained perfectly free from bromine, as that obtained even at the boiling-point of sulphur still contained a little bromine. This seemed to add some weight to the theory of the existence of a definite compound of sulphur and bromine, a little of which might be retained by the sulphur; but as I have now succeeded in obtaining perfectly pure sulphur as a residue of the distillation of the mixture, and have, moreover, succeeded in finding a reason why the high-boiling residues retained bromine, I propose to give an account of the experiments which have led to these

results. On passing pure dry air over $S_{32}Br_{50}$ at the temperature of the laboratory, a varying distillate was found, as shown in my last paper, and I now find that on varying the temperature, the distillate and residue were found to vary with the temperature in such a way as to show increased dissociation with increased temperature. When the current of air is passed long enough (as the distillate always contains more bromine than SBr) and the residue becomes rich in sulphur, the excess of that substance crystallises in very beautiful transparent yellow needles. These crystals are, of course, of the prismatic form, and many of them, on being slightly pressed with a penknife blade, turned opaque throughout their entire length, owing to their being transformed into the octohedral modification. The formation of these crystals does not take place in a very regular manner, as the liquid in which they are formed seems to be like a supersaturated solution, and any disturbing cause may accelerate the formation of the crystals. Thus two vessels of the same size and form were placed side by side in a vessel, and equal weights of the mixture placed in them, and dry air passed over them. Crystals of sulphur appeared in one vessel five days before the other, but when the residue consisted of nothing but sulphur, that in which crystals first appeared contained 2 per cent. more of residue. Thus, although the following table shows the general result of dissociation increasing with temperature, it is not likely that any exact formula could be drawn up for its progress, owing to these disturbing causes:—

Time.	Temperature.	Mixture taken.	Distillate.	Residue.
420 hours	15°	5·2750	5·2485	0·0265
507 „	18°	6·1425	6·0910	0·0315
543 „	25°	6·8520	6·7800	0·0720
462 „	36°	5·2250	5·1430	0·0820
325 „	43°	4·8270	4·6845	0·1425
602 „	49°	6·3145	6·1475	0·1670
435 „	60°	6·0025	5·8100	0·1925

The sulphur in the residue contained not the slightest trace of bromine, so that here, even at the temperature of 15°, was complete dissociation. Of course when the mixture contains more bromine, the amount of residue is less. The reason why the high-boiling residue contained bromine appears to be this:—When sulphur is heated in contact with bromine, it retains its elementary character so thoroughly as to pass through the various states when heated, so that when the portion boiling about 230° is poured into water, a substance exactly resembling plastic sulphur is obtained, but containing some bromine. Whether this is a compound of plastic sulphur or not could, I think, be determined only by calorimetric relations; but if it were, the equiva-

'lent of this modification would be very high, as the compound contains only 3 or 4 per cent. of bromine. It is then the passing of the sulphur into these viscous modifications which causes it to retain the bromine with such tenacity.

IV.—*On the Determination of Lithia by Phosphate of Soda.*

By C. Rammelsberg.

Berzelius detected the lithia in the Carlsbad water by evaporating the solution of the alkalis with phosphoric acid and carbonate of soda. On treating the whole with water an insoluble phosphate of soda and lithia remained on the filter.

In a paper on lithia-salts I showed (*Pogg. Ann.*, **66**, 79) by synthetic experiments that this substance was a mixture of the phosphates of lithia and soda, containing variable quantities of the two alkalis, corresponding with the formula $(Li,Na)_3PO_4$. These observations were contradicted by Mayer (*Ann. Chem. Pharm.*, **98**, 93), who asserted the non-existence of the double phosphate, the precipitate being pure Li_2PO_4, if caustic soda be added instead of carbonate. But repeating my former experiments (*Pogg. Ann.*, **102**, 441) I confirmed them entirely, and I obtained the same results by the analysis of amblygonite (*Monats. d. Akad. Wiss.*, Berlin, 1872, 153).

In an interesting paper on lithia-micas, Berwerth (*Tschermak min. Mitth.*, 1877, 337), employed the method of Mayer, and found much more lithia than those chemists who had analysed lithia-micas before him. As I intended to repeat these researches, I resolved to repeat also the former experiments. Definite quantities of sulphate and of chloride were treated with phosphate of soda and caustic soda, but the weight of the insoluble phosphate was in all cases much greater than it would have been as pure phosphate of lithia; and the analyses of these substances showed that they were composed of lithia-phosphate and soda-phosphate, containing the two salts in the proportions of 3 : 1 and 9 : 2 molecules.

These results confirm all my former observations; they prove that lithia cannot be determined by the method of Mayer, recommended also by Fresenius.

V.—*On the Composition of Lithia-micas.*

By C. Rammelsberg.

In consequence of the important crystallographical and optical researches on the micas by Tschermak, many new analyses of these minerals have been made. Berwerth published (*Tschermak Mitth.*, 1877, 337) his researches on the lithia-micas of Rozena, Paris in Maine (U.S.), and Zinnwald, the first and the third of these micas having already been analysed by other chemists. The differences between the new and the former analysis concern only lithia and soda:—

Rozena.

Lithia.	Soda.	
1·27	1·30	per cent. (Cooper).
1·28	1·25	„ (Rammelsberg).
5·88	—	„ (Berwerth).

Zinnwald.

1·60	1·41	per cent. (Lohmeyer).
2·41	0·71	„ (Stein).
1·27	0·39	„ (Rammelsberg).
3·28	0·42	„ (Berwerth).

As stated in the former paper, Berwerth determined the lithia by phosphate of soda, taking the precipitate as Li_3PO_4, whereas according to my own experience, it is under all circumstances a mixture of Li_3PO_4 and Na_3PO_4.

With regard to my former researches on micas, I found it necessary to repeat the analyses of lithia-micas, taking the greatest care in determining the alkalis. Berwerth found great difficulty in obtaining the alumina free from lithia: the precipitation by ammonia must therefore be repeated several times. The potassium-platinum chloride contains no lithia, for its analysis gave numbers near the calculated. The separation of lithia and soda was effected by treating the chlorides with ether-alcohol, as I proposed long ago.

It is well known that the lithia-micas contain larger quantities of fluorine than any other species of mica; but do they also contain the elements of water? On melting the well-dried mineral in a platinum tube with carbonate of potash and soda, a small quantity of water appears, and may be collected in calcium chloride, but it does not seem to be an essential constituent of the micas of this series:—

I. *Rozena.*

	Berwerth.	Rammelsberg.
Fluorine	7·88	7·12
Silicic acid	50·98	51·70
Alumina	27·80	26·76
Oxide of manganese	0·05*	1·29
Magnesia	—	0·24
Lime	—	0·40
Potash	10·78	10·29
Soda	—	1·10
Lithia	5·88	3·75†
Water	0·96	0·30
	104·33	102·95

II. *Paris, Maine (U.S.).*

	Berwerth.	Rammelsberg.
Fluorine	5·15	5·60
Silicic acid	50·39	(50·39)‡
Alumina	28·19	28·43
Potash	12·34	10·89
Soda	—	0·75
Lithia	5·08	4·04§
Water	2·36	1·12
	103·51	101·22

III. *Juschakowa, Ural.*

That beautiful mica was analysed by Rosales in 1843 (*Pogg. Ann.*, **58**, 154).

	Rosales.	Rammelsberg.
Fluorine	10·22	8·71
Silicic acid	48·92	48·98
Alumina	20·30	21·67
Oxide of manganese	4·67	5·36
Lime	0·12	—
Potash	10·96	11·08
Soda	2·23	0·54
Lithia	2·77	4·88
Water	—	0·66
	100·19	101·88

* FeO. † 3·62 and 3·87 were found in two experiments.

‡ For want of pure mineral, Berwerth's number is here taken.

§ Found: 4·09 and 3·98.

IV. *Zinnwald.*

	Berwerth.	Rammelsberg.
Fluorine	7·94	7·62
Silicic acid	45·87	46·44
Alumina	22·50	21·84
Peroxide of iron	0·66	1·27
Protoxide of iron	11·61	10·19
Protoxide of manganese	1·75	1·57
Magnesia	—	0·18
Potash	10·46	10·58
Soda	0·42	0·54
Lithia	3·28	3·36
Water	0·91	1·04
	105·40	104·63

Calculating my analyses, the atomic ratio is—

	R′	:	R̶	:	Si.	
I.	2·0	:	1	:	3·2	(2 : 1 : 3).
II.	1·9	:	1	:	3·0	(2 : 1 : 3).
III.	2·3	:	1	:	3·3	($2\frac{1}{3}$: 1 : $3\frac{1}{3}$).
IV.	3·6*	:	1	:	3·5	($3\frac{1}{5}$: 1 : $3\frac{1}{5}$).

Hence I deduced the formulæ—

$$\text{I. II.} \left\{ \begin{array}{l} n\mathrm{R'_2\cancel{R}Si_3O_{10}} \\ \mathrm{R'_2\cancel{R}Si_3Fl_6} \end{array} \right\}$$

n being = 15 in I, = 18 in II.

$$\text{III.} \left\{ \begin{array}{l} 10(\mathrm{R'_{14}\cancel{R}_6Si_{20}O_{65}}) \\ \mathrm{R_{14}\cancel{R}_6Si_{20}Fl_{130}} \end{array} \right\}$$

$$\text{IV.} \left\{ \begin{array}{l} 12(\mathrm{R'_6R''_2\cancel{R}_3Si_{10}O_{34}}) \\ \mathrm{R'_6R''_2\cancel{R}_3Si_{10}Fl_{68}} \end{array} \right\}$$

Lithia-micas are combinations of bi- and singulo-silicates (oxysilicates) isomorphously mixed with analogous fluosilicates. The silicates are:—

$$\text{I. II. } \mathrm{R'_8Si_3O_{10}} = 2\mathrm{R'_2SiO_3} + \mathrm{R_4SiO_4}.$$
$$\text{III. } \mathrm{R_{10}Si_4O_{13}} = 3\mathrm{R'_2SiO_3} + \mathrm{R'_4SiO_4}.$$
$$\text{IV. } \mathrm{R'_{14}Si_5O_{17}} = 3\mathrm{R'_2SiO_2} + 2\mathrm{R'_4SiO_4}.$$

* R″ = 2R′.

VI.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF TÔKIÓ, JAPAN.

(1). *On the Red Colouring Matter of the Lithospermum Erythrorhizon.*

By M. KUHARA, Assistant in the Chemical Laboratory.

THE Japanese give the name "Shikon" (*i.e.*, purple root) to the root of the *Lithospermum erythrorhizon*, which is found in commerce in the form of thick lumps of a beautiful purple colour on the outside, but yellowish-white within. It was formerly largely used for dyeing "Tokio purple," but on account of the fugitive character of this colour, and from the recent introduction of aniline colours, its use has been almost entirely abandoned.

Approximate analysis of the air-dried root gave the following results:—

Moisture.....	15·75	per cent.
Ash	11·36	,,
Glucose	9·93	,,
Invert sugar	3·92	,,
Aqueous extract.....	21·13	,,
Alcoholic extract	14·68	,,

The aqueous solution contained, besides sugar, a green colouring matter, which could be precipitated by lead acetate, but was not further examined. Almost the whole of the red colouring matter was found in the alcoholic solution, and possessed properties closely resembling those assigned to the colouring matter of alkanet, *Anchusin*, to which Dr. Bolley gave the formula $C_{35}H_{40}O_8$ (p. 384, *Crooke's Dyeing and Calico-Printing*). In some of its colour-reactions the pure colour under examination differs considerably from those of anchusin, while the composition, given hereafter, does not at all agree with that found by Dr. Bolley.

The colouring matter was first prepared by the method recommended for anchusin. The root was cut into small pieces, and exhausted with water, after which it was dried and treated with alcohol; the blood-red alcoholic solution was acidulated with a little hydrochloric acid, and the alcohol distilled off. The colouring matter thus obtained was found to be still impure, and in order to purify it more thoroughly, the alcoholic solution was mixed with an aqueous solution of basic lead acetate. The precipitate so formed was allowed to stand for about 12 hours, then filtered and washed with cold water. It was

then suspended in cold water and decomposed by a current of sulphuretted hydrogen; and the precipitate was allowed to settle, washed, dried, and exhausted with alcohol, which dissolved the colouring matter. On evaporation, the colouring matter was left behind in a nearly pure state.

It thus forms a dark, resinous, uncrystallisable mass, having a beautiful green metallic reflection. It is soluble in alcohol, ether, benzene, oil of turpentine, methylic alcohol, and bisulphide of carbon, but not to any extent in water. It has a feebly acid reaction, and a peculiar odour. When heated it first softens about 95°, and then partially volatilises in red fumes, which condense on the colder part of the tube.

The alcoholic solution has a peculiar absorption spectrum closely resembling that of an alcoholic extract of alkanet. Its alcoholic solution gives the following reactions:—

Alkalis	Change the purple colour to blue.
Acids	,, ,, red.
Baryta-water.....	Gives a beautiful violet precipitate.
Stannous chloride.....	Completely decolorises the solution.*
Stannic chloride	Gives a deep reddish-purple precipitate.
Cupric sulphate.....	Gives a purple coloration.
Ferric chloride	Gives a dark-green coloration.
Aluminic acetate	Gives a bright-purple colour, and on standing a slight precipitate.
Silver nitrate	Gives a slight red precipitate.
Chlorine-water	Decolorises the solution on boiling.
Lead acetate	Gives a purple precipitate.
Basic lead acetate.....	Gives a purple precipitate, which turns blue on the addition of an excess.

An ultimate analysis of the colouring matter gave the following results:—

	Found.	Calculated for $C_{20}H_{30}O_{10}$.
Carbon.....	54·82	55·8
Hydrogen	7·60	7·0
Oxygen (difference)	37·58	37·2
	100·00	100·0

* An alcoholic solution of alkanet gives with stannous chloride a crimson precipitate: a point of difference between it and the colouring matter under investigation.

Barium Salt.—This was prepared by precipitating the alcoholic solution of the colouring matter with baryta-water. The purple precipitate so obtained was slightly soluble in water, which assumed a slight purplish tinge; the precipitate was carefully washed with cold water, and dried. It then bore a close resemblance to indigo, having a dark purple colour with bronze reflection. It is soluble in ether, and also to a slight extent in alcohol.

A determination of the barium oxide gave the following number:—

	Found.	Calculated for $C_{20}H_{28}BaO_{10}$.
Barium oxide	27·7	27·26

which leads to the formula $C_{20}H_{28}BaO_{10}$ for this salt.

Having on hand some quantity of the barium salt, it was desired to remove the barium, and so obtain the purified colouring matter, and to this end various plans were tried, but without success. The following method was thought at first to give satisfactory results, but it was afterwards found that the colouring matter had undergone a change in chemical composition. The barium salt was first dissolved in ether, the ethereal solution mixed with about twice its volume of moderately strong chlorine-water, and the mixture violently agitated. The lower aqueous layer was found to contain barium, and the upper ethereal layer left on evaporation a shining brown scaly substance. Elementary analysis gave the following numbers:—

	Found.	Calculated for $C_{20}H_{30}O_{15}$.
Carbon	47·08	47·06
Hydrogen	6·084	5·88
Oxygen	46·836	47·06
	100·000	100·00

By the action of dilute nitric acid upon the original colouring matter a substance was obtained, whose chemical and physical properties were similar to those of the substance obtained by the action of chlorine-water upon the barium salt. On boiling some of the finely powdered colouring matter with dilute nitric acid, it gradually changed, with slight effervescence, to a brown mass which floated on the surface of the liquid. After boiling for a considerable time, the residue was separated, washed thoroughly with water, and dissolved in alcohol. This solution, after filtration, left on evaporation a brownish scaly substance having the following percentage composition:—

Carbon	46·866
Hydrogen.....	6·250
Oxygen.....	46·884
	100·000

It is, therefore, probable that these two bodies have the same composition, represented by the formula $C_{20}H_{30}O_{15}$, formed from the original colouring matter by addition of five atoms of oxygen.

Bromine-compound.—When the finely powdered colouring matter was mixed with excess of bromine, a violent reaction occurred, considerable volumes of hydrogen bromide being evolved. After standing for some time, a black pasty substance was formed, which was first washed with water, then dissolved in alcohol, and the blood-red solution thus obtained evaporated to dryness on the water-bath.

A dark brownish-red substance was thus left, which had a peculiar odour, and was soluble in ether and alcohol. It was not decomposed by boiling with strong nitric acid, so that to estimate the bromine it was necessary to fuse with potassic nitrate and carbonate. The mean of several analyses gave 48·33 per cent. bromine.

By combustion the following numbers were obtained:—

	Found.	Calculated for $C_{20}H_{25}Br_5O_{10}$.
Carbon	30·45	29·09
Hydrogen.....	3·26	3·03
Bromine.....	48·33	48·48

It thus appears to be a compound in which five atoms of hydrogen of the original colouring matter have been replaced by five atoms of bromine.

Chlorine-compound.—When the finely divided colouring matter was mixed with pentachloride of phosphorus, a violent reaction took place, and a black mass was formed. After remaining at rest for 24 hours, the excess of pentachloride was decomposed by the addition of water, and the residual mass was thoroughly washed with water. It was then dissolved in alcohol, and the solution after filtration was evaporated to dryness. A black resinous substance was left behind, soluble in alcohol. The chlorine was determined by fusion with potassic nitrate and carbonate, and precipitation with silver nitrate, but the result is probably too low:—

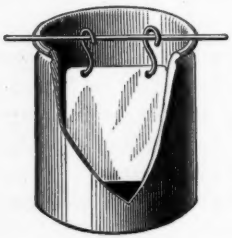
	Found.	Calculated for $C_{20}H_{28}Cl_2O_{10}$.
Carbon	49·08	48·09
Hydrogen	5·72	5·61
Chlorine.....	12·90	14·22

Further experiments are now in progress with a view to ascertain the nature of this colouring matter.

VII.—*Researches in Dyeing.* Part I: *Silk and Rosaniline.*

By Edmund J. Mills, D.Sc., F.R.S., "Young" Professor of Technical Chemistry in Anderson's College, Glasgow, and George Thomson.

I. The combination of colouring matters with silk, wool, cotton, and mordants, while in itself but a branch of chemical combination in general, nevertheless presents some features of peculiar interest. It also constitutes a field almost entirely new to the investigator, though the subject is one of the oldest in chemistry, and from a technical point of view it is a topic of very considerable importance. We have therefore undertaken the examination of several of the problems connected with dyeing, at first, and more particularly, inquiring into the nature of the transaction which occurs when a vat is exhausted of its tinctorial ingredients. In order to obtain primary results, we carried out our experiments at the ordinary temperature, dealing with what appeared to be an elementary case, viz., the combination of silk with rosaniline.



Scale ½.

II. The apparatus which was employed is illustrated in the accompanying figure. It consists of an ordinary earthenware pot, across the rim of which lies centrally, and sunk flush, a glass rod; to this are attached two glass hooks, which support the piece of silk beneath the level of the liquid.

The silk employed was "white" ribbon, free from wool and cotton. It contained a little Prussian blue, having been freed from which it yielded 12·5 per cent. of water and an inappreciable amount of ash. 4,556 square millimeters of this silk weighed ·3447 gram.

Although we tried various methods of estimating the quantity of rosaniline deposited, no direct process succeeded in our hands; we therefore had recourse to the portable colorimeter, contrived by one of us for such measurements (*Proc. Phil. Soc. Glasgow*, **10**, 310), and determined the amount of rosaniline salt remaining in solution. The probable error of a single determination was about ·67 per cent. "An experiment" was carried out in the following manner:—A number of pots, rods, and hooks having been prepared, a uniform volume of a standard solution of rosaniline salt was placed in each pot, and enough water added to make up 450 cub. centims.; the pots were then

immersed in running water for at least half-an-hour. Pieces of the prepared silk of almost exactly equal weight, and previously steeped in water, were now immersed, one in each pot, and the above set left under close cover, still in the bath of running water, for a definite interval x of time. At the end of the interval x, the silk was removed from the first pot, and the amount of residual colouring matter ascertained by at least twenty-five determinations; the second pot was similarly treated at the end of the interval $2x$, and so on. As the temperature was practically constant, we are thus able to ascertain the rate of the exhaustion of the vat in a particular case. This last statement, indeed, requires occasional reservation. So great is the intensity of the attraction between rosaniline and silk, that it is much modified by very slight and, in our case, uncontrollable fluctuations in the experimental conditions. A horizontal wrinkle in the piece would, by the change induced in the convection at the surface of the silk, be quite adequate to account for considerable variations from any theory based on a supposed uniform set of events. We must also bear in mind that to effect the uniform action of a solid in a liquid still remains to a great extent an experimental problem.

III. The chemical nature of silk is deserving of more profound investigation than it has hitherto received. So far as can be judged from what has as yet been done, it is an "amido-acid," capable of combining with either alkaline or acid bodies; and its formula is based on the remarkable C_6 modulus, so frequent among animal and vegetable products (*Chem. Soc. J.*, 1878, **1**, 69).

Rosaniline is known to us, through the classical researches of Hofmann, as a tertiary triamine, itself colourless, and whose polyacid solutions are also nearly colourless, while the mon-acid salts are red to red purple with increasing dilution.* One possible cause, therefore, of the loss of colour by a rosaniline solution in silk dyeing might be the formation of a rosaniline silk-compound by part of the rosaniline, the rest of the rosaniline forming a colourless salt with the hydric chloride, etc., hereby set free. We find, however, that this cannot be the case. In an actual experiment, ·00077 gram of the monohydrochloride (a quantity relatively comparable with what we used) dissolved in 450 c.c. of water, required about 1·32 gram of hydric chloride, as strong aqueous solution, in order to bleach it; the amount of hydric chloride necessary to convert it into trihydrochloride is only ·00017 gram. The liberation of hydric chloride cannot, then, be an efficient cause of the loss of colour.

We have also been careful to work, at present, at the ordinary temperature. For at the heat of boiling water a solution of rosaniline

* This effect is very prettily seen when a white disk—a crucible-lid, for instance,—is slowly raised through a weak-red solution to very near the surface.

hydrochloride or acetate undergoes more or less complete dissociation, attended of course, by loss of colour. Thus, for example, if a solution of either of those salts, containing ·0000003 gram in 1 cub. centim., be boiled for half-an-hour, complete decoloration ensues. But a piece of purified silk, immersed in the liquid, is almost immediately dyed red. We thus have the remarkable phenomenon, admirably suited to illustrate dissociation for a lecture, of silk being dyed red with a colourless solution of magenta.

By this method we can easily collect mere traces of acid bodies from large volumes of solution.

We have also inquired into the problem, whether the salt is deposited as a whole, or only in part, upon silk. To 400 cub. centims. of pure water ·021 gram of the hydrochloride was added, and the whole raised to about 100°; purified silk was then immersed, until, after prolonged contact, all colour had disappeared in the cold. The silk was then removed. The supernatant liquid gave scarcely a perceptible opalescence with silver nitrate; water of the same hydrochloric strength produces an abundant turbidity. Hence we infer that the silk becomes red by virtue of the deposition of the salt as a whole.

IV. Considering the above change as a chemical process, we have now to express it in symbols. Each of the miniature vats may be regarded as a system, in which all the conditions but one are kept constant; and that one—the colour combination, namely—corresponds with a very small transposition of weight. The relation between the amounts of colouring matter remaining after successive equal intervals of time, will therefore be a logarithmic relation; and this will be of a twofold character, inasmuch as the separate and independent effects of the solvent and the silk are jointly measured. The equation then is—

$$y = A\alpha^x \pm B\beta^x \quad (1),$$

where y is the amount of colouring matter remaining after a time x, the total initial amount being $(A \pm B)$; α and β being geometric factors, depending respectively on the action of the silk and the solvent. We shall find, in the sequel, that β may $= 1$, 0, or a fraction; so that the equation (1) may become—

$$y = A\alpha^x \pm B \quad (2), \text{ or}$$
$$y = A\alpha^x \quad (3).$$

We shall always regard $(A \pm B)$ as 100.

Rosaniline Acetate.

V. The specimen worked with was beautifully crystallised, and apparently pure; it was weighed after drying at 100°.

Experiment A.—Mean weight of silk, ·3585 gram; rosaniline salt, ·000595 gram; mean temperature, 7·7°; unit of time, 23·7 hours.

$$y = 100(\cdot 7887)^x.$$

x.	y Found.	y Calc.
0·00	100·00	100·00
1·00	78·56	78·87
1·85	64·74	64·46
2·86	50·80	50·72

Probable error of a single comparison of theory with experiment, 0·17.

VI. *Experiment B.*—Silk, ·1825 gram; rosaniline salt, ·000595 gram; temperature, 8·2°; unit of time, 24 hours.

$$y = 99{\cdot}87(\cdot 7687)^x.$$

x.	y Found.	y Calc.
0	100·00	99·87
1	74·90	76·77
2	60·43	59·01
4	34·85	34·87

Probable error of a single comparison, 0·91.

So far as may be judged from these two experiments it appears that an elevation of 0·5° C. more than compensates for (approximately) halving the weight of the silk. [Compare the remarks at the end of § II.]

Rosaniline Hydrochloride.

VII. The salt was in well-formed crystals, but somewhat slow of solution; the weights of it that are given were not very accurately ascertained, but they are strictly comparable one with the other.

Experiment A.—Silk, ·3791 gram; rosaniline salt, ·000825 gram; temperature, 2·9°; unit of time, 24 hours.

$$y = 83{\cdot}77(\cdot 7209)^x + 16{\cdot}23.$$

x.	y.	y Calc.
0	100·00	100·00
1	76·54	76·62
2	59·79	59·77
3	47·60	47·61

Probable error of a single comparison, ·03. According to this experiment, 16·23 per cent. of the hydrochloride would at the low temperature of the experiment have remained permanently in the liquid; or, ·000693 gram of that salt would have been affected by ·3791 gram of silk.

VIII. *Experiment B.*—Silk, ·3829 gram; rosaniline salt, ·00055 gram; temperature, 5·9°; unit of time, 24 hours.

$$y = 145{\cdot}12(\cdot 8220)^x - 45{\cdot}12.$$

x.	y.	y Calc.
0	100·00	100·00
1	74·36	74·16
2	52·16	52·92
4	21·13	21·13

Probable error of a single comparison, ·31. Since, when $y = 0$, $x = 5{\cdot}96$, nearly, it follows that the liquid would in this case have been completely decolorised after about 143 hours. A rise in temperature and a diminution in the amount of rosaniline salt have changed the sign of the constant B.

IX. *Experiment C.*—Silk, ·3446 gram; rosaniline salt, ·000784 gram; temperature, 12·4°; unit of time, 12 hours.

$$y = 123{\cdot}2(\cdot 7816)^x - 50(\cdot 5)^x.$$

x.	y.	y Calc.
0	100·00	[73·20]
1	71·34	71·29
2	61·55	62·76
3	53·83	52·57
4	52·88	[42·85]
5	37·77	34·37
6	26·44	27·30
7	23·21	21·56
8	16·88	17·00

It is evident that (0) and (4) are failures; the equation has been calculated from the remaining figures. Excluding the two failures, the probable error of a single comparison is 1·18.

X. The following triple experiment (D) was undertaken to ascertain the influence of alkaline chlorides on the dyeing of silk with rosaniline salt. Silk, ·3690 gram; rosaniline salt, ·00077 gram; temperature, 12·2°; sodium chloride, 1 gram; potassium chloride, 1 gram; unit of time, 24 hours. The equations are—

Blank ..... : $y = 65{\cdot}09(\cdot 3080)^x + 34{\cdot}52$
With sodium chloride .... : $y = 70{\cdot}47(\cdot 5338)^x + 29{\cdot}53$
With potassium chloride.. : $y = 70{\cdot}86(\cdot 5075)^x + 29{\cdot}14$

	Blank.		With sodic salt.		With potassic salt.	
x.	*y.*	*y* Calc.	*y.*	*y* Calc.	*y.*	*y* Calc.
0.....	100·00	99·61	100·00	100·00	100·00	100·00
1.....	54·50	54·57	67·18	67·15	64·37	65·10
2.....	41·99	40·70	56·36	49·61	47·39	47·39
3.....	36·20	36·42	40·01	40·25	35·50	38·40
4.....	33·73	35·11	29·37	35·25	33·57	33·84
Probable error of a single comparison	0·66		3·02		1·01	

The experiments with sodium salt are not as satisfactory as could be desired, the potassium salt giving as usual the better result.

Taking our work so far into consideration, we have arrived at the following conclusions:—

(1.) That when silk is dyed with rosaniline salt, that salt is deposited as a whole.

(2.) That a boiling weak solution of rosaniline salt may undergo dissociation so as to become quite colourless; in which state, however, the dissociating force is wholly overcome by silk.

(3.) That for periods of four days, at the ordinary temperature, a magenta-vat is exhausted at compound interest.

(4). That the rate of exhaustion of a magenta-vat is retarded by sodic or potassic chloride, and not improbably to an equal extent by equal weights of those chlorides.

The further development of these researches is in progress.

VIII.—*Note on two New Vegeto-Alkaloïds.*

By Baron F. von Mueller and L. Rummel.

Alstonine.—Alkaloïd of the bark of *Alstonia constricta* (F. v. M.). This alkaloïd is obtained by treating the alcoholic extract of the bark with water and a little hydrochloric acid; adding to the filtered solution a small excess of ammonia; dissolving the separated flocks in ether; and evaporating the ethereal solution. The alkaloïd then remaining is purified by again dissolving in dilute acid, and repeating the above process.

Alstonine is an orange-yellow, brittle, pellucid mass of very bitter taste; it melts below 100°, and is carbonised at higher temperatures; dissolves easily in alcohol, ether, and dilute acids, sparingly in water,

University of Michigan

All its solutions in the dilute state exhibit a strong blue fluorescence, which is not affected by acids or alkalis. Its alcoholic solution has a slightly alkaline reaction. Alstonine combines with acids, but does not completely neutralise them. Hydrochloric and other strong acids, also alkalis, decompose it partially on evaporation on the water-bath to a dark-coloured, viscid, acid substance. The hydrochloride gives precipitates with the chlorides of platinum and mercury, the iodides of potassio-mercuric, and of potassio-bismuthous iodide; also with biniodide of potassium, phospho-molybdate, and phospho-tungstate of sodium, bichromate of potassium, picric acid, and with the alkalis and alkaline carbonates. Tannic acid does not precipitate the hydrochloride, but gives a precipitate with acetate and with the pure base. Concentrated nitric acid dissolves alstonine with crimson colour, becoming yellow on warming; sulphuric acid with reddish-brown colour, changing to dirty green; hydrochloric acid forms a yellowish solution. Alstonine differs from ditamine chiefly by its behaviour towards concentrated acids and by its fluorescence, which has not been recorded of the other alkaloïd.

Duboisine.—This is a volatile alkaloïd obtained from the leaves and twigs of *Duboisia myoporoïdes* (R. Br.), and probably identical with the piturine found by Staiger in *Duboisia Hopwoodii*. It is prepared like nicotine—and is a yellowish, oily liquid, lighter than water, of a strong narcotic odour resembling that of nicotine and of cantharides; has a very strong alkaline reaction, and neutralises acids completely; dissolves in any quantity of ether, alcohol, and water, throws down ferrous oxide from ferrous sulphate; dissolves without colour in concentrated acids. Its hydrochloride, which is a deliquescent salt, when greatly diluted by water, is precipitable by biniodide of potassium, by potassio-mercuric and potassio-bismuthous iodide, and by tannic acid, but not by any other of the usual alkaloïd reagents.

Nicotine, which duboisine resembles, is distinguished from the latter by its specific gravity, its less powerful odour, and by its hydrochloride; and by being precipitable in a diluted aqueous solution by phosphomolybdate of soda, picric acid, and chloride of platinum.

IX.—*A Chemical Study of Vegetable Albinism.*

By A. H. Church.

The phenomenon of vegetable albinism or albication here considered, must not be confounded with *chlorosis*, the pallor of imperfect chlorophyllation, and the usual accompaniment of etiolation; nor is it identical with *icterus*, a defect of coloration due to absence of iron, and promptly remedied by the administration of traces of a ferric salt.

In the autumn of 1877 I began some experiments upon the white leaves and white parts of leaves of certain variegated plants. It might be thought that there was nothing easier than to obtain abundant supplies of these materials for analysis; but such is not the case. Very few plants can be employed for this study: for either the quantities of material obtainable in an isolated state are inadequate, or it is found to be impracticable to secure, from the same plants, both white and green portions of precisely the same age, and grown under the same conditions. The common ribbon grass, *Phalaris arundinacea*, affords an example of the first difficulty; several kinds of variegated Pelargonium illustrate the second. My earlier set of experiments was made upon three species of plants, all admirably adapted for the purpose, for in each the white and green parts were at once abundant and strictly comparable. The three species laid under contribution last year were—

Acer Negundo	Gathered	September	17th
Ilex Aquifolium	„	„	24th
Hedera Helix	„	October	4th

In every instance the leaves were gathered without the intervention of knife or scissors, and were at once transferred to well-closed bottles previously weighed; thus no loss of water could occur during transit to the laboratory.

The water, the organic or combustible matter, and the ash were first of all determined; the results, translated into percentages, are here given :—

	Acer Negundo.		*Ilex Aquifolium.*		*Hedera Helix.*	
	White.	Green.	White.	Green.	White.	Green.
Water.....	82·83	72·70	74·14	62·83	78·88	66·13
Organic matter	15·15	24·22	23·66	35·41	18·74	31·63
Ash.....	2·02	3·08	2·20	2·47	2·38	2·24

Thus the white leaves of these three plants showed an average of 10 per cent. more water than the green leaves, while the dry organic matter in the former was not quite two-thirds of that present in the latter. The ash from the dry matter was more abundant in the white than in the green leaves.

	Percentages of ash.	
	White.	Green.
Acer Negundo.....	11·76	11·28
Ilex Aquifolium.....	8·51	6·52
Hedera Helix.....	11·27	6·61

The nitrogen and the matters soluble in ether were determined in the dry matter of holly and ivy with the following results:—

	Per cent. nitrogen.		Per cent. ether extract.	
	White.	Green.	White.	Green.
Ilex	2·28	·85	6·77	6·83
Hedera....	2·76	2·35	6·12	9·65

These figures may best be studied in connection with the more complete data derived from the second series of experiments.

It is in the ash analysis that the most remarkable differences in composition between the white and green leaves were noticed. More potash and more phosphorus pentoxide were invariably found in the white parts than in the green, while they were almost always poorer in lime:—

	Percentage composition of Ash of—					
	Maple.		Holly.		Ivy.	
	White.	Green.	White.	Green.	White.	Green.
K_2O.....	45·05	12·61	35·30	16·22	47·20	17·91
CaO.....	10·89	39·93	21·50	34·43	12·92	48·55
MgO	3·95	4·75	3·23	2·43	1·11	1·04
Fe_2O_3.....	—	—	3·11	3·11	2·62	2·31
P_2O_5.....	14·57	8·80	9·51	7·29	10·68	3·87

There is here no indication that the presence of chlorophyll in the green parts involves a higher percentage of iron.

We may now proceed to the description of the second series of experiments performed in the summer and autumn of the present year. Thanks to the permission of Sir J. W. Hooker, and to the obliging attention of the officials at Kew, I was enabled to make successful use of the Jodrell Physiological Laboratory in the Royal Gardens. My

experiments were further aided by a grant from the Government Research Fund.

Four exotic plants were the subjects of my renewed inquiry. The specimens of variegated plants submitted to analysis were gathered with every precaution :—

Elæagnus pungens	On July 17th.
Plectogyne variegata	„ 9th.
Cyperus alternifolius	„ 10th.
Alocasia macrorhiza	In October and November.

Of the Elæagnus several sprays of wholly white and of wholly green foliage were used : the white and green parts were separated by rending from five leaves of Plectogyne : part of the Cyperus specimens were entire white or green leaves, part similarly coloured portions of leaves.

I give the results of my experiments on these leaves in the same order as that previously followed in recounting the results of the 1877 series—

	Elæagnus pungens.		*Plectogyne variegata.*		*Cyperus alternifolius.*	
	White.	Green.	White.	Green.	White.	Green.
Water	69·49	63·24	74·60	69·72	77·35	71·72
Organic matter	28·98	34·65	22·25	27·42	20·02	25·53
Ash	1·53	2·11	3·15	2·86	2·63	2·75

It will be seen that the white leaves and parts of leaves of all three plants contain on an average 5·58 per cent. more water than the green leaves and parts of leaves. The percentages of ash in the dry substance of the leaves of each of the three plants were as follows :—

	White.	Green.
Elæagnus pungens	5·01	5·74
Plectogyne variegata	12·39	9·44
Cyperus alternifolius	11·63	9·76

The dry leaves of these plants were not obtainable in sufficient quantities for an exhaustive analysis of each, but a more complete study of the Elæagnus than of the others was made. Still the nitrogen in each specimen was determined, the results being here given :—

	Nitrogen in dry substance. White.	Green.
Elæagnus pungens	4·24	2·82
Plectogyne variegata	2·23	2·39
Cyperus alternifolius	1·94	2·04

Something more will have to be said presently about the nitrogen in Elæagnus, but as a whole the preceding figures do not indicate any definite divergence between white and green leaves, so far as their percentages of nitrogen are concerned.

The ashes of the three plants were analysed with care, although the quantities of materials at my disposal did not admit of a complete study of each specimen.

The following table gives the percentage composition of the ash of —

	Elæagnus pungens.		*Plectogyne variegata.*		*Cyperus alternifolius.*	
	White.	Green.	White.	Green.	White.	Green.
Potash.....	60·93	31·31	39·54	34·46	48·54	24·20
Lime.....	6·35	31·50	19·95	24·00	6·05	10·81
Magnesia.....	?	?	2·35	2·94	?	2·89
Ferric oxide.....	2·23	·77	?	?	?	?
Phosphorus pentoxide ..	14·02	10·20	7·62	4·59	7·09	7·34
Silica.....	4·56	2·25	·35	?	36·75	46·03

On comparing these figures with those obtained in 1877 in the analysis of the ash of white and green leaves of maple, holly, and ivy, observe the following three features in common:—

1. The ash of the white leaves contains much more potash than that of the green leaves.

2. The ash of the white leaves contains much less lime than that of the green leaves.

3. No deficiency of iron in the white leaves has yet been detected.

Further evidence, corroborating these and previous statements as to the main chemical differences between white and green leaves, is afforded by a second series of analyses just made of white and green maple leaves, and by an analysis of a wholly white leaf of *Alocasia macrorhiza*, and also of a wholly green leaf from the same species, though not from the same individual plant, both the latter specimens having been grown in the water-lily house at Kew. I give partial analyses of the dry matter of these two gigantic Aroïd leaves, with more complete examinations of their ash and of the ash of the maple leaves gathered in 1878:—

In dry matter.	*Alocasia macrorhiza.* White.	Green.
Total nitrogen	3·45	2·98
Nitrogen in albuminoïds	1·16	2·10
Nitrogen, as nitrates, &c.....	2·29	0·88
Albuminoïds	7·35	13·38
Ash.....	23·89	15·01

In 100 parts of ash of—

	Acer Negundo (1878).		*Alocasia macrorhiza.*	
	White.	Green.	White.	Green.
Potash	54·44	13·03	60·48	38·07
Lime.....	8·50	40·16	19·37	20·37
Magnesia.....	3·22	—	—	2·77
Ferric oxide	—	—	—	—
Phosphorus pentoxide	14·87	7·38	13·08	6·89
Silica	·68	1·31	—	—

The most striking results here relate to the nitrogen in the white Alocasia leaf, nearly 70 per cent. of this element existing in non-albuminoïd and but partially elaborated forms, whereas in the green leaf less than 30 per cent. is in a similar condition.

I will now describe some additional experiments made with *Elæagnus pungens*, the only plant besides the maple of which I was able to obtain a supply at once fairly abundant, and yet entirely fulfilling the necessary conditions of comparison.

From physiological considerations, I was led to inquire more particularly into these three points:—

1. Amount of matters soluble in ether in the two kinds of leaves.
2. Proportion of albuminoïd to total nitrogen.
3. Presence of calcium oxalate and carbonate. I throw the results of this further inquiry into a tabular form:—

Percentages of	In dry matter of leaves of *Elæagnus pungens.* White.	Green.
Matters extracted by ether	2·63	6·05
Albuminoïd nitrogen	1·83	1·81
Non-albuminoïd nitrogen.....	2·41	1·01
Calcium oxalate	·41	2·10
Calcium carbonate	traces	decided traces

(1.) It was natural to expect that the absence of chlorophyll from the white leaves would lower their per cent. of matters soluble in ether; in fact, they yield to this solvent less than half the amount that is given by the green leaves. This result was obtained only when pure

ether, free from both alcohol and water, was employed in the extraction-apparatus. When ordinary ether, neither dry nor free from alcohol, was used, the percentages of dissolved matters were 4·62 from the dry green leaves, and 3·28 from the dry white. But it was clear that some chlorophyll still remained in the green leaves, while some substances, not soluble in pure ether, had been extracted from the white. Unless we could assume that the amounts of resin, wax, oil, &c., are the same in the dry matter of both sorts of leaves, it would be hazardous to assert that the difference between the two ether extracts (6·05 — 2·63 = 3·42) represents the percentage of chlorophyll in green Elæagnus leaves when dry.

(2.) In determining albuminoïd nitrogen in white and green leaves, I used the method, which I originated some five years ago, of curdling the proteid matter by means of carbolic acid solution. In some plants leaves dried in the water-oven give precisely the same percentages of albuminoïd nitrogen in the residue when washed with water, as the fresh leaves of the same plant furnish when the carbolic process is adopted. In such cases the soluble albumin of the leaf has been rendered insoluble in water by the heat of the water, just as effectually as by the carbolic solution aided by metaphosphoric acid. The following determinations of nitrogen are in close agreement with those in the Alocasia leaves:—

	Percentage in dry matter of Elæagnus leaves.	
	White.	Green.
Total nitrogen	4·23	2·82
Nitrogen by carbolic process	1·83	1·81
Albuminoïd nitrogen in residue insoluble in water.....	1·82	1·83
Non-albuminoïd nitrogen	2·40	1·01

Thus, nearly 60 per cent. of the nitrogen in the white leaves is non-albuminoïd, while just over 30 per cent. is the proportion in the green leaves.

(3.) The third special question to which I have been endeavouring to obtain an answer is that concerning the form or forms of combination in which the lime is present in the two sorts of leaves. With one doubtful exception, lime is decidedly less abundant in the white leaves than in the green. Now I found, in the case of Elæagnus, that the percentages of lime salts soluble in water, cold and hot, were practically equal in the dry matter of the white and of the green leaves, but that both carbonate and oxalate were present in notable quantities in the latter, and almost absent from the former. Analysis gave:—

	Percentages in dry matter of Elæagnus leaves.	
	White.	Green.
Lime in soluble salts	·28	·31
Lime as oxalate	·18	·92
Lime as carbonate	trace	·50

From these numbers it is clear that the great excess of lime found in the green leaves, when compared with the white, is mainly due to the physiological process, of which calcium oxalate is the final product, although a part of that excess must be attributed to the simple deposition of calcium carbonate drawn up by the roots in solution in the soil-water, and left behind on the transpiration of moisture from the leaf. From the white leaves, albeit they contain more water, the transpiration is probably less, since, through the absence of chlorophyll, they can hardly be the seat of the production of carbon-compounds, and of the various changes attendant upon that process.

Before summing up the chief results of the present inquiry and endeavouring to correlate them with the phenomena of vegetable albinism, it will be useful to cite an analysis of two other plants, namely, of a parasite and its host. I chose for this purpose the common dodder (*Cuscuta Trifolii*) and the red clover, on which it was living. Like the white parts of variegated leaves, the dodder is destitute of chlorophyll. Moreover, by the aid of its haustoria, it brings its several tissues into intimate connection with the corresponding structures of the supporting plant, and so draws its nourishment almost wholly from the latter. The samples of the two plants, both in flower, were gathered simultaneously on the 15th September, 1878, care being taken to collect representative specimens. The analyses gave :—

	In 100 parts of—	
	Cuscuta Trifolii.	*Trifolium pratense.*
Water	87·39	81·10
Organic matter	11·45	17·59
Ash	1·16	1·31
	In 100 parts of the ash of—	
	Cuscuta Trifolii.	*Trifolium pratense.*
Potash.....	48·00	26·43
Lime	3·47	38·40
Magnesia	2·88	13·07
Phosphorus pentoxide	9·59	9·61

It will be observed that in the more aqueous character of the parasitic plant, and in its greater richness of potash, as well as in its low percentage of lime, we have points of agreement with albino foliage, while the vegetable host may be compared with green leaves.

If we further compare with white leaves those parts or organs of plants which live at the expense of other parts, we shall find close analogies between them. In short, if we determine the water, the organic substance, and the constituents of the ash in each of the following cases, we shall be able to affirm generally that white leaves are related to green pretty much as immature leaves to mature, tubers to foliage, petals to green bracts, vegetable parasites to their hosts. The white leaf may in fact be said to be parasitic on the green: it may be a warehouse, but it is not a factory. There seem to be present therein all the materials by the aid of which the organic compounds of the leaf should be constructed, but the constructive faculty or impetus is lacking. Lime compounds are, it is true, found, but sparingly, in most white leaves, but then the lime compounds in mature foliage are in great part a sign and relic of past activities. Perhaps it may be found that some minor ingredient other than those to which I have referred in the present paper, may be deficient or wanting in the white leaves. Further analyses are requisite to decide this point. But, after all, some structural or histological defect may be the real cause of the want of constructive power in the white leaves—of their lack of chlorophyll. Comparative microscopic examination and minute measurements of white and green portions have been made, but no real insight into the matter has thus been obtained. Often, as in the maple, the white portion of a leaf has but two-thirds of the thickness of the green; often a fluted or constricted aspect is caused by the imperfect development of the white tissues, as in the white borders of some Pelargonium leaves and the white stripes of some grasses. It has been further observed that the variegated and albino plants and shoots are usually smaller, more susceptible of injury by frost, and generally weaker than the normal green foliage. And when a variegated plant does throw out a wholly green shoot it grows with greater vigour than the rest of the plants. It has long been known that an albino cutting cannot be struck. Endeavours to stimulate the development of albino foliage in variegated plants, and to cause such plants to revert to the normal forms by chemical treatment of the soil, have not yet been attended with decisive results. Yet no decided structural defects accompany these slight peculiarities. But I hope another season to study this subject with further appliances and by new methods. I hope to measure the exact relations of equal areas of white and green foliage to carbon dioxide, oxygen, and moisture, and shall endeavour to see what results the injection into the vessels of white foliage of solutions of various organic and inorganic bodies may achieve. This summer I tried a few experiments of this kind with a measure of success, using the needle and syringe of hypodermic injections, and instantly closing the puncture with a drop of collodion. Thus several cubic centimeters

of the desired solutions were introduced beneath the epidermis of some Echeveria leaves, forming beneath the epidermis a gigantic blister, the contents of which were absorbed in a few minutes on exposing the plant to sunshine. Various colourless compounds becoming coloured by oxidation or reduction were employed; so also was lithium citrate, the course of which could easily be followed by subsequent dissection, drying, and spectroscopic examination of the various parts thus prepared. This use of lithium citrate, which I had the pleasure of introducing to Dr. McNab's notice some years ago, has yielded some valuable results in his hands and in those of certain foreign observers. I now find it quite possible to employ it on living plants without injuring their development. It is evident that it may enable us to learn something of the relations between the various parts of plants, and may aid in solving the question of vegetable albinism. But for all this physical work I must await the sunshine of another year.

A word about the ash analyses in the present paper. In a good many instances the figures are derived from a single determination, often necessarily made with a very small quantity of material. If a formula were to be established, such analyses, though performed in many cases with microscopic crucibles and other vessels, and with the aid of an exquisite assay balance, would be inadmissible. But they at least admit of certain general deductions being drawn, for they point without an exception in the same direction.

The nitrogen and ash analyses of the second series have nearly all been made by my assistant, Mr. C. Rawson.

X.—*On a Hydride of Boron* (*Preliminary Notice*).

By Francis Jones, F.R.S.E.

I am not aware that any attempt has been made since 1809 to obtain boron hybride. In that year Davy stated that a gas, which he supposed to be a compound of boron and hydrogen, was evolved by the action of water on potassium boride; and he obtained a similar gas by the action of acids on a boride of iron prepared by heating a mixture of boracic acid and iron filings to a high temperature. These results have been attributed to impurities in the substances employed, and it is generally stated that boron is the only non-metallic element which forms no compound with hydrogen.

Thinking it probable that a hydride might be obtained by other

reactions, I attempted in the first place, to obtain magnesium boride by the action of sodium on a mixture of magnesium chloride and potassium borofluoride, thus imitating the process employed for the preparation of silicon hydride. A very violent reaction occurred on simply mixing the substances, but no successful result was obtained on adding hydrochloric acid to the product.

It then occurred to me that magnesium boride might be obtained more simply, by strongly heating a mixture of magnesium dust and boron trioxide. On trying the experiment in the proportions suggested by the equation—

$$B_2O_3 + 6Mg = 3MgO + B_2Mg_3,$$

I found the action succeeded perfectly, and a grey friable mass was obtained, containing magnesium boride. When hydrochloric or nitric acid is dropped on this substance, great heat is given out, and an inflammable gas is evolved, which is without doubt a hydride of boron. On repeating the experiment on a larger scale, I obtained the gas in sufficient quantity to make the following observations. It is a colourless gas, burns with a bright green flame, and has a very disagreeable odour, resembling both that of phosphine and that of stibine. It is soluble to a slight extent in water; the solution gives with silver nitrate a brownish-black precipitate, containing both boron and silver. The gas is decomposed by passing it through a red-hot tube; but I have not yet obtained it unmixed with hydrogen.

The reaction of magnesium on boron trioxide also serves very conveniently for the preparation of boron itself. Half the quantity of magnesium represented in the above equation is used, and the product when extracted with hydrochloric acid, leaves amorphous boron as a brown powder.

XI.—*On the Occurrence of certain Nitrogen Acids amongst the Products of Combustion of Coal-gas and Hydrogen Flames.*

By Lewis T. Wright.

The only cases of combustion discussed in the following paper are those of coal gas and hydrogen burning in the air; and they are treated according to the preconceived theory that the origin of the nitrogen acids found combined with ammonia amongst the products of combustion is to be sought in the ammonia, either free or combined, that seems to be a constituent of a normal atmosphere. It has frequently

been noticed that ammonium nitrite is one of the products of combustion of hydrogen flames burning in the air; and Zoeller and Grete have recently confirmed this statement with regard to its formation, even when the hydrogen and air employed were specially purified by an elaborate process, consisting of a washing through two bottles containing potassium permanganate, two potash-tubes, and two tubes containing pumice stone saturated with sulphuric acid. Even then the condensed water contained minute quantities of ammonium nitrite.

It will not be out of place to mention here my experience with regard to the action of dilute solutions of ammonium nitrite at boiling temperatures. It is this: that when a certain degree of concentration is reached, continued boiling causes a considerable loss of ammonium nitrite, and that a portion of the salt thus lost is found in the distillate when the operation has been conducted in a retort fitted with an efficient condenser; and further, that all traces of this compound are not removed from such dilute solutions by boiling until dryness is reached. The experimental data which have led to these conclusions belong to a separate inquiry which is now being prosecuted.

Some time ago I noticed that the products of combustion of coal-gas contained both ammonium nitrate and nitrite, and the experiments first made were with coal-gas. The apparatus used for condensing the condensable combustion-products was similar to the well-known apparatus used by the London Gas Referees for determining the amount of sulphur in the coal-gas of the metropolis.

The amounts of the respective acids (nitric and nitrous) found are expressed in weight of nitrogen per 1,000 litres of gas consumed. It is believed that these acids were always combined with ammonia.

In the first series of experiments every precaution was taken to secure the gas employed from any trace of ammonia, but no attempts were made to purify the air used, which was, however, guarded from accidental contamination with ammonia.

TABLE I.—*Coal-gas free from Ammonia burned in a Normal Atmosphere with Bunsen Burner.*

	Nitrogen as HNO_3 per 1,000 litres coal-gas consumed.	Nitrogen as HNO_2 per 1,000 litres coal-gas consumed.
(1.)	·0009 gram.	·00096 gram.
(2.)	·00062 „	·0005 „
(3.)	·00056 „	·00061 „
(4.)	·00046 „	·00064 „
(5.)	·00035 „	·0002 „
Average	·00058 „	·00058 „

In the next case, the gas before being burned was passed over concentrated liquor ammoniæ. The presence of ammonia in the flame and its cooling effect were most marked.

TABLE II.—*Coal-gas charged with Ammonia burned in Normal Atmosphere with Bunsen Burner.*

	Nitrogen as HNO_3 per 1,000 litres coal-gas consumed.	Rate of consumption per hour.	Nitrogen as HNO_2 per 1,000 litres coal-gas consumed.
(1.)	·01346 gram.	27·5 litres	·00161 gram.
(2.)	·01044 „	28·3 „	·00184 „
(3.)	·01072 „	29·2 „	·00184 „
(4.)	·01067 „	29·5 „	·00161 „
(5.)	·00827 „	39·1 „	·00150 „
Average	·01071 „	30·7 „	·00168 „

These experiments were repeated with the air-holes of the Bunsen burner completely closed.

TABLE III.—*Coal-gas charged with Ammonia burned in Normal Atmosphere. Air-holes of Bunsen's Burner closed.*

	Nitrogen as HNO_3 per 1,000 litres coal-gas consumed.	Rate of consumption per hour.	Nitrogen as HNO_2 per 1,000 litres coal-gas consumed.
(1.)	·02141 gram	21·8 litres	·00315 gram.
(2.)	·01853 „	22·7 „	·00335 „
(3.)	·01217 „	27·2 „	·00161 „
(4.)	·01167 „	—	·0014 „
Average	·01595 „		·00238 „

Taking into consideration the rates of consumption, it will be found that closing the air-holes of the burner did not cause variation in the amounts of nitrogen acids formed.

In the next table will be found the amounts of nitrogen as nitric and nitrous acids formed when the air used for combustion was charged with a tolerably large quantity of ammonia. The gas consumed was free from ammonia. The means employed for charging the air with ammonia was that of placing round the top of the burner a number of small lumps of sesquicarbonate of ammonia. Under these circumstances the condensed water contained a large quantity of ammonium carbonate, and the air at the outlet of the apparatus was strongly alkaline.

TABLE IV.—*Coal-gas free from Ammonia burned in an Atmosphere charged with Ammonia. Bunsen Burner.*

	Nitrogen as HNO_3 per 1,000 litres coal-gas consumed.	Rate of consumption per hour.	Nitrogen as HNO_2 per 1,000 litres coal-gas consumed.
(1.)	·04645 gram	16·1 litres	·13154 gram.
(2.)	·04165 „	16·4 „	·11793 „
(3.)	·04485 „	18·6 „	·12701 „
(4.)	·03684 „	19·5 „	·10433 „
(5.)	·03363 „	20·3 „	·09522 „
(6.)	·03283 „	22·1 „	·09298 „
Average	·03938 „	18·8 „	·1115 „

The amount of nitrogen transformed from ammonia into nitric and nitrous acids by the agency of coal-gas flames controlled by the previous experimental conditions depends upon the rate of consumption. This is probably due to the diminishing air supply, the supply of air increasing, not in a direct ratio with the rate of consumption, but according to the square root of the difference of the temperatures of the inlet and outlet of the apparatus. This was very slight, owing to the efficiency of the condensation.

Some experiments were made with hydrogen flames, in order to see whether condensed water could be obtained by the combustion of hydrogen free from nitric and nitrous acids.

Cases in which hydrogen was passed over strong sulphuric acid and burned in an ordinary atmosphere, gave amounts of nitrogen varying between ·009 gram and ·018 gram for nitric acid, and not exceeding ·0002 gram for nitrous acid, per 1,000 litres of gas consumed. When, however, the air was previously purified by passing through 60 centimeters of pumice saturated with concentrated sulphuric acid, and two wash-bottles charged with a solution prepared by adding strong sulphuric acid to potassium permanganate, the condensed water did not contain any appreciable amount of nitric acid, and but very minute traces of nitrous acid, not exceeding ·00001 gram per 1,000 litres of hydrogen consumed.

By interposing between the pumice and wash-bottles a cylinder containing 60 centimeters of freshly-slaked lime, and by passing the hydrogen through two wash-bottles containing a solution similar to that used for purifying the air, condensed water was obtained by the combustion of the hydrogen, in all cases free from appreciable traces of nitric and nitrous acids. The condensed water did not develop the slightest tint with Griess's metaphenylenediamine in 24 hours, and had no action upon potassium iodide and starch in presence of hydrochloric acid.

These circumstances lead to the belief that the origin of the nitrogen acids found in the condensed water procured by burning coal-gas and hydrogen in the air, is ammonia, either free or combined.

XII.—*The Processes for Determining the Organic Purity of Potable Waters.*

By C. Meymott Tidy, M.B.

The determination of the organic matter in potable waters, both as regards its quantity and its quality, has been a subject of late years (as the Fellows of the Chemical Society are aware) productive of much discussion—of much difference of opinion—and (to use a mild phrase) of much warmth of feeling. I should be glad if I could lead and urge the discussion in a strictly scientific groove, unfettered and unimpelled by that warmth of feeling which has in this, as in many other questions, more often retarded than helped the attainment of that scientific accuracy to which we hope and desire that all our work and all our discussions should tend. Be this as it may, I trust that nothing I may say will be regarded in any other light than a desire to discuss fairly the position of water analysis, and the value to be attached, in my opinion (which I am by no means dogmatic enough to believe must be right), to the various processes employed by water analysts.

I am afraid the public *have* taken note and *are* taking note of chemists' differences, and distrust our work accordingly. Nor indeed is their distrust to be wondered at, deeply as it is to be lamented. To clear up these differences, chemists must be prepared not merely to criticise, but to study other processes besides their own, and accurately to compare results. An attempt to do this is the chief object of my paper.

The processes for estimating the organic matter in water, naturally divide themselves under two great heads:—

1. Where the organic matter is estimated from a water residue.
2. Where it is estimated in the original water, *i.e.*, from the water itself, and not from the residue after evaporation.

At this point I will venture to make one general remark, the correctness of which (whatever views we may hold as to possibility or impossibility) will, I think, scarcely be disputed, viz., that if it be possible by any process or processes to estimate the organic matter in the original water, such processes must have manifest advantages over

those where the quantity of organic matter is deduced from a residue. I will not here discuss this point further (for the proposition seems self-evident), save to add that the many very ingenious contrivances recommended by Dr. Frankland in evaporating a water for a combustion experiment, prove that he is as fully aware as any one can be of a source of error, which, except for the minute precautions he advises (precautions, let me say, not one whit too minute), would be likely to be not inconsiderable.

I. The Processes in which the Organic Matter is Estimated from a Water Residue.

(*a.*) *The Ignition Process.*

This process presupposes three things.

(α.) That no organic matter is lost, and none gained during the evaporation of the water.

(β.) That all the organic matter is burnt off by the ignition of a residue.

(γ.) That nothing but organic matter is lost by ignition.

But in all three points the process fails.

With respect to the actual loss of organic matter by evaporation, the only point to which attention need be particularly directed here, Dr. Frankland notes the fact that when urea is present in a sewage contaminated water, it is partially dissipated during evaporation in the presence of sodic carbonate, and that then, to use his own words, "a portion of the organic impurity of a water may be lost before the determination of *the organic and other volatile matter* is made." But apart from this one illustration, given by Dr. Frankland, considering that sodic carbonate is not a very unusual constituent of water—considering the subtle nature of the organic material with which we have to deal—considering how very little we know either of its actual nature or of its chemical characters and relationships—considering, moreover, that the organic matter of one water may not be the organic matter of another, or of any other water (for I would note that the very varied relative quantities of organic carbon and nitrogen recorded by Dr. Frankland to my mind clearly indicates an almost infinite variety in the character of the organic impurity itself)—considering, in short, that our knowledge of this organic impurity is practically *nil*, is it any stretch of the imagination to suppose, although we may have no very definite experiments in proof, that a part of the organic matter, and that, perhaps, the most important, although by no means a constant part, is dissipated or destroyed at the temperature (perhaps even at a much lower temperature), required to effect the vaporisation of the

water? Let me suppose, for example, that a water contained hydrocyanic acid (and the water poison seems at times to be as virulent in its action as prussic acid), where would this be after evaporation was complete?

On this point I will quote Mr. Wanklyn's words:—"In evaporating a water to dryness, destruction of the organic matter occurs during the evaporation. Some of the organic substances present in drinking water are very perishable, and others, doubtless, are almost indestructible when exposed for several hours to the action of air and moisture, at temperatures not exceeding 100° C. The few milligrams of organic matter contained by a litre of drinking waters are probably in no single instance preserved absolutely intact in the residue left on evaporating a litre of water down to dryness. In some cases, indeed, not the one-thousandth part of the organic matter originally present in the water will survive the evaporation."—(Wanklyn's reply to Dr. Frankland's paper before the Chemical Society, February 17, 1876.)

Nor indeed is it a stretch of the imagination to suppose that the mere mechanical removal of organic particles may be effected during evaporation. Many cases of a similar kind may be noted. A family, for instance, remove into a newly painted house. Before long they all show symptoms of lead poisoning. By what means, we may ask, did the lead get into their systems? Not, surely, by the actual vaporisation of the metal, but rather by the inhalation of solid lead particles, their detachment being coincident with, and the result of, the evaporation of the turpentine in the paint. In cases of fever all physicians recognise the necessity of removing the excreta as soon as possible from the sick room. Why? Because the mechanical propagation, in fact the carriage into the air, of the fever poison (be it germ or anything else) is probably effected by and along with the evaporation, slow though it may be, of the watery element. Without multiplying instances of a similar kind, I must acknowledge that these difficulties are very considerable, and suggest not unimportant objections to any process where the organic matter is estimated from a residue. And, moreover, this subject may be regarded from another and from an opposite point of view, *i.e.*, not the question of *loss*, but of *gain*: for, unfortunately, laboratories are not the most cleanly places in the world, and dirt will find its way, take what precautions you please, into every crack and crevice. I confess, therefore, to a doubt whether any process can be considered universally applicable, where the estimation of the organic matter is made from a water residue, firstly, because there may be a *loss* of the actual organic matter present in the water during evaporation, such loss being either chemical, physical, or mechanical; and secondly, because there may be a *gain* resulting from the introduction of extraneous organic matter.

I will here give analyses of four waters, in two of which the loss on ignition was very great, although judged by the actual absence of colour, or by at most a slightly blue tinge when examined in bulk in a 2-foot tube, and by the absolute persistence for three hours of the pink tint produced by the merest trace of potassic permanganate, they may be regarded to have been as nearly as possible free from organic matter. I could multiply these cases if necessary, but I have selected these four, as waters of vastly different character. The results are stated in grains per imperial gallon of 70,000 grains.

Colour in tube.	Total solids.	Ammonia.	Oxygen required to oxidise.	Loss by ignition.	Lime.	Magnesia.	SO_3.	Silica.	Cl = NaCl.	Hardness.		$N = HNO_3$.
										Before boiling.	After boiling.	
										°	°	
Blue...	51·33	0·006	None..	12·32	12·60	1·023	10·70	1·16	6·54 = 10·78	32·5	21·0	1·44 = 6·48
Blue...	20·33	0·003	None..	1·61	8·64	0·341	0·764	0·67	0·678 = 1·12	17·5	2·5	0·414 = 1·86
Blue...	140·50	0·000	None..	8·43	57·70	2·121	78·69	0·67	0·248 = 0·41	—	—	0·089 = 0·40
Blue...	22·00	0·001	None..	1·32	8·88	0·614	0·705	0·50	1·286 = 2·12	17·0	1·5	0·472 = 2·12

I conclude with one or two remarks on those cases where the indications afforded by the ignition process may prove of value:—

1. *In the analysis of sewage* I have always been in the habit of stating the loss on ignition. In such cases we have no nitrates (or next to none) to contend with, and the results we obtain by ignition may be taken as a coarse approximate indication, not perhaps so much of the extent of purity, as of the extent of impurity.

2. The *blackening of a water residue* when ignited indicates, of course, the presence of organic matter. Such an experiment affords, according to some, a rough indication of the quantity of organic matter present. I am by no means certain whether the eye, beyond a certain point can, taking all things into consideration, recognize degrees of blackening. For instance, say of two waters, that one contained double the quantity of total solid matter present in the other water, in order to obtain the same degree of blackening, the organic impurity must be twice as much in the heavier water as in the lighter. The fact is, the degree of blackening is largely influenced by the sub-division of the organic matter, and therefore by the amount of the total solid matter present. This much then, I think, is all that can be said on this point:—if there are no signs of blackening, the absence (more or less complete) of organic matter may be inferred; but if there are signs of blackening on ignition, beyond the fact that the water contains organic matter, no opinion can be given as to quantity.

3. *The smell evolved by the ignition of a water residue* often reveals important facts. It is impossible to describe these in detail. I am quite sure no one could mistake the smell evolved on incinerating a sea-water residue. Further, the odours of residues containing large quantities of animal and vegetable organic matter when ignited are perfectly distinctive, and in many cases it is quite practicable to say the kind of animal organic matter present. I need not discuss this further. Its application depends on two things—*the one*, a matter more or less within our power, viz., constant practice; *the other*, a matter scarcely within our power, viz., delicacy of smell.

(*b.*) *The Combustion Process.*

The details of this process, invented by Dr. Frankland and Dr. Armstrong, have been on more than one occasion brought before, and must be perfectly familiar to, the Fellows of the Chemical Society (*Chem. Soc. J.*, **21**, 77). The process consists in evaporating a given quantity of water to dryness, means being adopted to get rid of the carbonates and nitrates, and estimating the organic carbon and nitrogen in the total solid residue by a combustion experiment.

The learned authors claim for this process that "it is the only method that affords any trustworthy information respecting the quantity of organic matter present in potable waters."

The objections urged against the combustion process are of a two-fold character—*first*, general; and, *secondly*, special.

The general objection is, to employ Mr. Wanklyn's term, its "impracticability," by which I suppose is meant (omitting the question of cost of apparatus) partly the manipulative skill required, and partly the length of time consumed in conducting the experiment. These two objections may seem to have some weight at first sight, but they have very little on further consideration.

As regards the fact that the process requires a certain amount of manipulative skill, it is admitted. Dr. Angus Smith, who speaks well of the process, adds, "When hands sufficiently delicate are found to do it." To construct a watch is a delicate operation, but he is no watch-maker who cannot construct a watch. It is the possession by practice of the manipulative skill of these trained hands which constitutes a man an analytical chemist, and for my part the sooner so delicate and difficult a work as water analysis is taken out of the hands of those who imagine themselves professional chemists after a few lessons in a laboratory, the better for chemistry and for sanitary medicine. This, then, as an objection is worthless. As regards the length of time required for the analysis, I confess I have no sympathy with those who are perpetually urging the adoption of a process because it can be performed in some extraordinarily short time. Of course ease and rapidity are points to be considered, all other matters (such as accuracy of results, delicacy, and such like) being equal. Accuracy and delicacy being unequal, ease and rapidity ought not to enter into the calculation.

The special objections, however, to the process require more careful thought:—

1. First of all we have the objection to any process for the estimation of organic matter necessitating the evaporation of the water to dryness. I have already discussed generally the importance I attach to this objection, and I have only a few further remarks to make here, suggested by the special details adopted by Drs. Frankland and Armstrong in their process. I do not know on what grounds Mr. Wanklyn makes the statement, but I may presume on good grounds, that in some cases not the one-thousandth part of the organic matter originally present in a water survives the evaporation. He adds, further, "If then the actual combustion itself were perfectly devoid of experimental error, it follows as a matter of necessity" (which, let me add, is obvious if his former statement be correct), "that the combustion process of water analysis must sometimes fail to measure

University of Michigan

$\frac{999}{1000}$ of the carbon and nitrogen existing in organic combination in drinking water."

I have already pointed out that gain and loss are both to be feared during evaporation. To prevent gain, Dr. Frankland adopts Professor Bischoff's ingenious contrivance of the bird-fountain, the dish being covered over with a glass shade (the bird-fountain is Bischoff's contrivance, and the covering of the capsule with a glass shade, Frankland's), the whole apparatus being so arranged that there is no need to disturb it during the entire evaporation. Admirable in every respect as it appears to me this arrangement is in preventing gain, I do not understand how it meets the difficulty of loss. And here I may mention, that Dr. Mills, an ardent supporter of the combustion process, remarks in his paper on potable waters that "*substantially* satisfactory evidence" (a very guarded expression) has been given that there is no material loss during evaporation. Very shortly after this cautious statement, Dr. Mills suggests what he regards as a slight improvement on Bischoff's arrangement (an improvement which as yet I have not tried, but intend to do so) which he terms "a convectionless feed," that is, instead of the delivery tube passing from the reservoir to the evaporating dish being straight, it is bent in two places, the consequence of which is that at the end of each regurgitation two long bubbles of air always remain entrapped. But now note the exact reasons why Dr. Mills thinks this an improvement. First of all, he remarks, that it prevents convection through the tube to the reservoir, and thus prevents loss of heat. But more than this (and here I will quote his exact words), "It is objectionable," he says, "to heat the delicate organic matter of waters, and especially of peaty waters, any longer than is strictly necessary." Surely here is the key to the cautiously guarded phrase, "substantially satisfactory evidence of no material loss."

But Dr. Frankland himself has by no means overlooked the possibility of losing volatile organic constituents during evaporation.* Let me refer, for instance, to a passage in Drs. Frankland and Armstrong's original paper (*Chem. Soc. J.*, **21**, 89). They are speaking in the text of boiling the water in an open flask for two or three minutes with sulphurous acid, when in a foot note they remark, "In operating with waters strongly contaminated with sewage, it is desirable that the flask in which this operation is performed

* I have already quoted Dr. Frankland's words when discussing the ignition process. He is remarking that urea is partially dissipated during evaporation in the presence of sodic carbonate, and adds these remarkable words, remarkable more especially when taken in conjunction with other statements: "Thus a portion of the organic impurity of a water may be lost before the determination of the organic and other volatile matter is made."

should be furnished with an inverted Liebig's condenser *in order to prevent the loss of volatile organic constituents* and ammonia." "It is true," Dr. Frankland adds, "with all ordinary waters this precaution is unnecessary." But I should like to ask what evidence Dr. Frankland has that it is unnecessary? Sewage water may be injurious we know. At any rate Dr. Frankland admits that it contains, or may contain, volatile organic constituents. Has Dr. Frankland any evidence to show that it is not that very volatile organic matter of which he treats in this foot-note, to which the poison of sewage may be due, and to which a water contaminated sometimes with a mere trace of sewage may owe its virulent and poisonous action? Remembering how virulent that poison is, I should myself be far from astonished if it were of a highly volatile nature, just as we know that arseniuretted hydrogen far exceeds arsenious acid in intensity of action on the human body.

As yet, then, no reply has been given to the question asked on a former occasion in this room by Professor Abel, "Are any organic matters, however small in quantity, carried off mechanically or oxidised during evaporation?" (*Chemical News*, March 10, 1876.) I admit the question is one of enormous difficulty to answer, but the *onus probandi* rests with those who assert that the water-residue contains *all* the organic matter present in the water. It is quite true, as Dr. Armstrong has remarked, "that in an evaporation performed under glass shades in a reducing atmosphere containing sulphurous acid, oxidation would be reduced to a minimum" (*Chemical News*, March 10, 1876), but then oxidation is not everything. Admit that oxidation is reduced to a minimum (he does not say entirely stopped, and the very substances may be oxidised that are the cause of the evil), there are still the dangers arising from mechanical conveyance, and from the chances of volatility. Pasteur's experiments, again, may be accepted, and of these Dr. Armstrong reminds us, but it must be remembered that the evils arising from drinking contaminated water are probably the work of invisible particles—germs or whatever else you like to call them—but at any rate of particles beyond the reach of balance or microscope. Until, then, we have definite evidence that no organic matter is oxidised, either by the oxygen dissolved in, or by the oxygen in contact with, the water (it is not enough to say oxidation is reduced to a minimum), and also that no organic matter is either volatilised or destroyed by the heat required for evaporation, it follows that evaporation must always constitute a possible source of error in any process, adopt what precautions you please, where the determination is made on the residue of such evaporation. Indeed we cannot resist the conclusion that after all our trouble, we may be simply estimating the harmless organic matter, while that which was

poisonous and disease-producing has been carefully got rid of by previous treatment.

2. Our next difficulty is an important one. Before being evaporated down, it is directed that the water should be boiled for a minute or so with a solution of sulphurous acid. This is done for the double purpose of expelling the carbonic anhydride combined and dissolved, the presence of which would interfere with the carbon determination, and also for the purpose of effecting the removal during evaporation of the nitrogen existing as nitrates and nitrites. A couple of drops of a solution of ferric chloride are also added before the evaporation is commenced in order to secure the complete expulsion of the nitrogen, the exact action of which, however, is not very clear.

Now respecting this action on the nitrates and nitrites, cases have occurred (not simply in my own analyses, but in those made by others) which lead me to doubt whether, without exception, complete reduction takes place under the conditions mentioned. And here I would note that in Dr. Frankland's experiments on artificial waters, performed for the purpose of proving the accuracy of the combustion process, he did not (at least I infer he did not, because he does not state otherwise) add any nitrate to the waters on which the experiments were conducted. The only other experiments I can find recorded bearing on this question are those of Professor Bischoff, made on Loch Katrine water mixed with different proportions of nitrates. I really think, however, that Professor Bischoff has proved a little too much, because he has shown that the more nitrates he added, the less organic nitrogen he obtained. Thus with Loch Katrine water, pure and simple, the organic carbon was 0·162, and the organic nitrogen 0·024. In a similar sample to which he added nitrates (he does not state how much), the organic carbon was 0·140 and the organic nitrogen 0·020, whilst in a third and similar sample to which he added a large quantity of nitrates, the organic carbon was 0·170, and the organic nitrogen 0·018.

I have myself made a very careful series of observations on this point, and I will endeavour briefly to state my results.

a. If the nitrogen as nitrates does not exceed 1·0 part per 100,000, that is a quantity equal to 3·150 grains of nitric acid per gallon, I have never been able to come to any other conclusion but that the reduction of the nitrates was complete on boiling the water with 20 c.c. or 40 c.c. (according to the quantity of nitrates present) of the sulphurous acid solution. The number of experiments I have made within this limit has been eight. When Dr. Frankland, therefore, argues, in support of his view, that although the Thames water contains the largest quantity of nitrates in the summer, nevertheless there is no evidence that the amount of organic nitrogen is thereby

affected, his argument is sound, although it must be distinctly borne in mind that the combined nitrogen in the Thames water falls enormously within the limit of 1 part in 100,000.

β. Supposing, however, that the nitrogen as nitrates exceeds this amount (that is, between 1·0 and 1·5 per 100,000), I have had cause to doubt how far boiling with sulphurous acid is sufficient to effect complete reduction, although 60 c.c. of the sulphurous acid solution was used. I speak with some diffidence on this matter, because sometimes the action seems complete, and sometimes not, and why I am unable to explain. However, this much I must admit, that whilst I have no reason to doubt the efficiency of the process when the nitrates are present in small quantity, I am by no means so certain of its efficiency when they are present in large quantities.

I am aware that when the nitrates exceed this amount, Dr. Frankland advises filling up the dish after evaporation is complete, with a 10 per cent. solution of sulphurous acid, using a quarter, half, or one litre, according to the quantity of oxidised nitrogen present.

I never do this part of the experiment without a feeling of despair at the possible result. Admitting that the addition of a sulphurous acid solution to the water itself does no harm, I cannot conceive that the organic matter in the residue can survive direct actual treatment with a sulphurous acid solution. Remembering that at least the solution must be acid if the nitrates are to be perfectly reduced, surely the oxidation of a part of the sulphurous acid is no far-fetched idea, and sulphuric acid being formed, I cannot see how we can overlook the possibility of the removal and destruction of some of the carbonaceous matter. Dr. Armstrong has said, "What if sulphuric acid be formed—allow that albuminoïds are broken up under the influence of dilute acids; at any rate more stable bodies are formed." This argument would be all very well if we knew of what the active organic poison of a water consisted. It may be that by the time our residue gets into the combustion tube, as I said before, much that we want to find, and which was present in the original water, has gone.

I confess this to be a difficulty:—add too little sulphurous acid, and the reduction of your nitrate is incomplete; add too much, and there is a possibility at any rate that your organic matter may cease to be.

3. Evaporation being complete, the next step is the combustion of the organic matter of the total solid residue. And here comes a difficulty of some importance, although by no means insuperable:—I mean obtaining pure cupric oxide, and the assaying of it. I am myself painfully aware how in this respect inconveniently large errors may arise, and I mention it as a difficulty, although not as an objection to the process.

Our combustion being complete, and the organic carbon and nitrogen

determined, Mr. Wanklyn contends that the results are valueless, on account of the small quantity of water *residue* operated upon, the error of experiment being, to use his own words, "so large as to render illusory the measurement of the organic carbon and nitrogen"—in other words he would state that the experimental error is greater than the whole quantity we are estimating. Dr. Frankland, on the other hand, contends that one-millionth of a gram of nitrogen and half a millionth of a gram of carbon are distinctly measurable quantities. Mr. Wanklyn, most unfortunately, in no way meets experiments by experiments. So far as I am able to judge, I confess that my own experiments of late confirm those of Dr. Frankland.

And now I should wish to say a few words on the process, treating it as a whole, and from a purely practical point of view. I must admit that in some respects I have altered my views, since I spoke on the subject some years ago in this room. I am convinced that the determination of the organic carbon is to be relied upon. Thus examining samples of the same water four times successively, I obtained in two experiments, 0·128 of organic carbon; in a third experiment, 0·130; and in a fourth experiment, 0·133. Another reason for altering my views I shall give directly.

But I am not convinced as yet that a similar accuracy can be attained in the estimation of the organic nitrogen. Of course the quantity present is often remarkably small, and always small compared with the organic carbon. I think, therefore, that Mr. Wanklyn's objection respecting experimental error must be allowed to have some weight in the determination of the organic nitrogen, if it has none in the determination of the organic carbon. The difficulty of reducing the nitrates and of effecting the complete expulsion of the nitrogen, the presence of ammonia, the possibility of occluded nitrogen in the copper, constitute a series of important possible errors, especially when taken in conjunction with the necessary experimental error, and with the very small quantity of material on which the determination is conducted. Moreover, I have certainly failed to get that marked uniformity of results in the case of the organic nitrogen that I have obtained in the case of the organic carbon.

I am far from desiring to suggest mere theoretical difficulties to the process. It has most certainly in my case so much improved on acquaintance, that I believe it to be a process of great value; nevertheless, speaking for myself, I must say that whilst I accept without the slightest hesitation the determination of the organic carbon, I cannot attach the same value to the determination of the organic nitrogen. At present, therefore, I must venture to doubt how far I should feel justified in allowing that, according to the ratio of the organic carbon and nitrogen, conclusive evidence can be obtained as

to the source of the organic matter—that is, whether it be vegetable or animal.

II. Processes in which the Organic Matter is Estimated from the Water before Evaporation.

(*a.*) *The Ammonia Process.*

The *principle* of the ammonia process (the ingenious invention of Mr. Wanklyn) consists in the comparative determination of the nitrogenous organic matter by the quantity of ammonia (called by him albuminoïd ammonia) yielded by the destruction of the organic matter. This destruction, as is well known, is effected by boiling the water in the presence of potassic permanganate and a large excess of caustic potash. "The ammonia process" (to quote Mr. Wanklyn's words) "is in fact a sort of combustion process with ammonia for the ultimate product" (Wanklyn's "Water Analysis," p. 25).

Mr. Wanklyn, for reasons shortly to be mentioned, in no way approves of the course many have adopted, of regarding the albuminoïd ammonia process as a means of estimating quantitatively the organic nitrogen.

The process dates back to 1867. Mr. Wanklyn claims that, as now worked, it differs in *no essential* particular from that described then (p. 24). I should regard this as a matter to be deplored rather than a subject for congratulation.

The process is far too well known to need description. I will only note one or two points, to which I shall have to direct attention hereafter.

Mr. Wanklyn advises that the so-called albuminoïd ammonia should be estimated from half a litre of water, but he is also of opinion that accurate results may be obtained with 100 c.c. "I have analysed," he says (p. 43 of "Water Analysis," 4th edition), "the same water on the two scales, and got the same results."

I should wish also to note Mr. Wanklyn's classification of waters. He divides them into three classes, according to the quantity of albuminoïd ammonia they yield, viz.:—

Class I. *Waters of Extraordinary Organic Purity.*

These waters yield from 0·000 to 0·05 part per million or mgm. per litre. (This is equivalent to 0·000 to 0·005 in 100,000 parts, or 0·000 to 0·0035 gr. per gallon.)

Class II. *Safe Waters.*

These waters yield from 0·05 to 0·10 part per million or mgm. per

litre. (This is equivalent to 0·005 to 0·010 part per 100,000, or 0·0035 to 0·007 gr. per gallon.)

Class III. *Dirty Waters.*

These waters yield from 0·10 part and upwards per million or mgm. per litre. (This is equivalent to 0·010 part per 100,000 and upwards, or to 0·0078 gr. per gallon and upwards.)

I have collected from different parts of Mr. Wanklyn's work on "Water Analysis" the following conclusions, justified, in his opinion, by the estimation of the chlorine and of the ammonia and albuminoïd ammonia in a water.

1. If the free ammonia present exceeds 0·08 part per million, recent contamination of the water with urine is indicated, the ammonia resulting from the conversion of urea into ammonic carbonate (p. 41). In such a case a great excess of chlorides may be expected.

2. If chlorine and free ammonia be absent, or be present in very small quantity only, whilst the albuminoïd ammonia is large in quantity but slow in coming over during distillation, vegetable contamination (which in Mr. Wanklyn's opinion is very injurious) is indicated (p. 41).

3. If a quantity of albuminoïd ammonia not exceeding 0·05 part per million be obtained from a water, such water may be regarded as organically pure, although the chlorine and free ammonia be large, the free ammonia not constituting an important element unless the albuminoïd ammonia exceeds the quantity named (p. 53).

4. If the quantity of free ammonia be small, the albuminoïd ammonia is not to be regarded as a reason for condemning a water unless it reaches 0·1 part per million (p. 54).

5. Apart from the quantity of free ammonia and of chlorine, the presence of 0·1 part per million of albuminoïd ammonia is to be regarded as suspicious, whilst if it reaches 0·15 part per million the water should be absolutely condemned (p. 54).

Notwithstanding these conclusions, the learned author of the process will pardon my reminding him that I think I remember a case not many months back where he recommended two waters as not unfit for a town supply, that contained, according to his own analysis, 0·14 and 0·2 part per million of albuminoïd ammonia.

The main objections raised to this process by Dr. Frankland with which I will deal first of all are—*first*, that the conversion of the nitrogen of the organic matter of water into ammonia is *never* under the conditions of the experiment (but it would perhaps be more accurate to say is *seldom*) complete; and *secondly*, that taking a series of nitrogenised bodies, the proportion of nitrogen converted into ammonia

varies widely. It is right to state that these circumstances were noted and recorded in the first instance by Mr. Wanklyn himself. These objections are worth considering:—

(α.) Some substances yield *the whole* of their nitrogen as ammonia when boiled in an alkaline permanganate solution, as, *e.g.*, piperidine, hippuric acid, narcotine, asparagine, piperine, &c.

(β.) Other substances evolve *two-thirds* of their nitrogen as ammonia, as, *e.g.*, albumin.

(γ.) Other substances evolve *one-half* of their nitrogen as ammonia, as, *e.g.*, morphine, strychnine, codeine, &c. Respecting strychnine, Mr. Wanklyn observes, "the missing half of the nitrogen in strychnine passes provisionally into the state of some volatile alkaloïd" (p. 157).

(δ.) Other substances evolve *one-third* of their nitrogen as ammonia, as, *e.g.*, kreatine.

(ϵ.) Other substances evolve *one-fourth* of their nitrogen as ammonia, as, *e.g.*, theine.

(ζ.) Other substances evolve *very little* of their nitrogen as ammonia, as, *e.g.*, uric acid. On this Mr. Wanklyn remarks, "possibly uric acid furnishes so small a proportion of its nitrogen as ammonia, owing to the existence of nitrogen in the ureic state" (p. 156).

(η.) Other substances evolve *none* of their nitrogen as ammonia, *e.g.*, bodies in which the nitrogen exists as a nitro-compound, as urea, picric acid, &c., where the whole of the nitrogen is expelled as gaseous nitrogen or as nitric acid; in explanation of which Mr. Wanklyn says, "urea is, in a sense, a perfectly oxidised substance, requiring the elements of water to transform it into carbonic acid and ammonia, and if simply oxidised would exhibit a deficiency of hydrogen: there would be CO_2 and only 4H along with 2N" (p. 156).

Dr. Frankland remarks, that from experiments, he finds that soluble peaty matter (the presence of which in water he regards, and in that I agree with him, as of comparatively little importance) yields a proportion of nitrogen as albuminoïd ammonia, varying from less than one-third to nearly one-half the total nitrogen present.

		Nitrogen per cent.	
		Theoretical.	Found by experiment.
Bodies yielding the whole of their nitrogen as albd. ammonia.	Asparagine	18·66	18·05
	Piperine	4·91	4·45
	Diamylamine chloride	7·24	6·53
	Amylamine	16·09	17·96
	Diphenyl-tartramide	9·33	8·41
Bodies yielding one half of their nitrogen as albd. ammonia.	Morphine	4·91	2·31
	Codeine	4·42	2·47
	Papaverine	4·12	1·81
	Strychnine (Wanklyn)	8·38	4·49
	[Do. (Frankland)], *Chem. Soc. J.*, Vol. **21**	„	2·65
	Iodide of methyl-strychnine	5·88	2·74
	Brucine	7·11	3·79
	Sulphate of quinine	7·51	3·71
	Do. (Frankland)	„	4·27*
	Sulphate of cinchonine	7·84	4·58
	Nicotine	17·28	8·89
	Naphthylamine	9·80	5·55*
	Toluidine	13·09	7·05*
	Acetate of rosaniline	11·63	5·30*
	[Narcotine (Frankland)]	3·38	1·55
Bodies yielding ⅔rds of their nitrogen as albd. ammonia.	Albumin	13·0—16·0	8·24
Bodies yielding ⅓rd of their nitrogen as ammonia.	Kreatine	32·07	10·38
Bodies yielding ¼th of their nitrogen as ammonia.	Thein	28·86	7·03
Bodies yielding very little of their nitrogen as ammonia.	Uric acid	33·33	5·76
Bodies yielding none of their nitrogen as ammonia.	Urea	46·66	0·00
	Picric acid	18·34	0·00

Dr. Frankland records 40 experiments on waters, in which both "the albuminoïd ammonia," and also the nitrogen by combustion, were estimated with the following results:—

(α.) In the majority of cases the nitrogen as albuminoïd ammonia showed a great deficiency over the nitrogen obtained by combustion. In 22 waters the nitrogen as ammonia, estimated in each water in

100,000 parts, gave a total of 0·169, whilst by combustion he obtained 0·534, or more than three times as much.

(β.) Sometimes, and more particularly when the nitrogen was present in small quantities only, the results accorded closely. Thus in 12 waters the nitrogen as albuminoïd ammonia was 0·045, whilst by combustion it was 0·044.

(γ.) Sometimes the nitrogen as albuminoïd ammonia showed an excess over that obtained by the combustion process. Thus in 6 waters the nitrogen as albuminoïd ammonia was 0·033, whilst by combustion it was only 0·012, or rather less than one-third (*Chem. Soc. J.*, **21**, 77).

No doubt there is a certain force in this objection. If the organic matter of all waters were alike, it would be of no importance whether the whole or only a definite part (be it one-half, two-thirds, or any other proportion) of the nitrogen of the organic matter was converted into ammonia. But inasmuch as in all probability the organic matter of one water is not the organic matter of other waters, each one in fact being different, the circumstance that bodies yield their nitrogen as albuminoïd ammonia in very, indeed in vastly, different proportions, constitutes an objection of some importance. Nevertheless I think that this objection may be overrated. If Mr. Wanklyn can show that his process indicates clearly that the yield of albuminoïd ammonia keeps pace with the purity or impurity, as the case may be, of waters, and that it is sufficiently delicate to indicate the finer grades of purity, I do not know that the circumstance that piperine yields the whole of its nitrogen as ammonia, that morphine yields one-half, that albumin yields two-thirds, and that thein yields one-fourth, has much value in a water analysis, whatever interest such facts of detail possess to the scientific chemist.

Mr. Wanklyn has so distinctly and repeatedly condemned the course taken by certain chemists in regarding his process as a method for the quantitative determination of nitrogen, that I think we should clearly remember that Mr. Wanklyn merely asserts that his process answers the question: Is this water wholesome or is it not? whilst it leaves untouched the question, How much organic nitrogen does this water contain? I agree with Mr. Wanklyn that these two questions are, for practical purposes, absolutely distinct.

Mr. Wanklyn's process has also been accused of yielding results which admit of no precise interpretation, inasmuch as it deals with bodies at present unknown (Dr. Mills on Potable Waters, *Chem. Soc. J.*, February, 1878). I am afraid this objection applies more or less to all processes.

In venturing to offer certain further criticisms on this process, I would first of all say a word or two on practical difficulties in the

details (for I am desirous of limiting myself as much as possible to the practical side of my subject) and afterwards treat the process as a whole.

1. I believe it to be practically impossible to prepare an alkaline solution of potassic permanganate absolutely free from ammonia. I have myself followed with the greatest precision the details given by Mr. Wanklyn for its preparation, and have moreover tried a large number of other means that have suggested themselves, such as fusing the potash before dissolving, and such like, without avail; nor have I ever found any permanganate solution made by others that was entirely free from ammonia. Hence it has always been necessary to estimate the quantity of ammonia in the permanganate solution, and to deduct this from the total amount obtained in the actual experiment.

2. I would note further the extreme difficulty, and more especially if organic matter be present in any excess, in effecting the complete decomposition of the organic matter, by merely boiling the water with the permanganate solution. Indeed I go so far as to express a doubt if complete decomposition can be effected by anything short of distillation to absolute dryness. Let me explain that, by *complete* decomposition, I mean as complete as the alkaline permanganate solution is capable of effecting. Let me illustrate what I mean. You distil a water with the permanganate solution until ammonia ceases to be evolved, and you then leave the apparatus for a few hours, carefully protecting it meanwhile from the contamination of a laboratory atmosphere, a danger Mr. Wanklyn does not admit. If you now distil the water once more you will find probably that the secondary yield of albuminoïd ammonia will be equal to, if not greater than, that obtained in the first instance; and so again and again fresh quantities of albuminoïd ammonia may be obtained until you have distilled over every drop of water in the retort. This fact has been noticed by several, and is referred to in a paper by Mr. Sidney W. Rich, published in the *Chem. News*, June 6, 1876. This, to my mind, is a very serious difficulty; because, considering the small difference that exists between the class of "waters of extraordinary purity" and the class termed by Mr. Wanklyn "*dirty waters*," a source of error of this nature becomes serious in the extreme. Indeed (speaking of experimental errors) this of itself is sufficient to account for one analyst (and I know a case in point) reporting a water to be of extraordinary organic purity, whilst a second reported the same water to be dirty water and entirely unfit to drink.

3. I should wish now to refer to a singular result that has occurred to me on several occasions in conducting the albuminoïd ammonia process. The permanganate solution is found by experiment, say, to contain a certain quantity of ammonia. On adding a given quantity of this test

solution to a water (the test solution being known, as I said, to contain a certain and estimated quantity of ammonia), it has been found that the total ammonia yielded by the test solution *plus* the water, is less than the ammonia known to be contained in the test solution itself. That is, as a matter of fact, there has been an actual disappearance of ammonia. I am not prepared to explain the cause of this, but I would suggest that, given a solution containing an excess of free alkali and a superabundance of active oxygen, you possess the conditions that are the most likely possible to bring about oxidation of the nitrogen. I am not suggesting this explanation moreover without certain other facts in support of it. In over 500 waters we have estimated the free ammonia in three different ways: *first*, in the original water just as it was; *secondly*, in a distillate, as advised by Mr. Wanklyn; and *thirdly*, in the original water, having first thrown down the lime salts by adding to the water a small piece of stick caustic potash. The results showed that in the latter case where an excess of alkali was present, and notwithstanding the almost absolute certainty that the piece of stick potash added was itself not entirely free from ammonia, the ammonia found was often considerably less than when it was determined from the water, either as it was, or in the distillate obtained from it. However this may be, the fact is certain that in some cases the albuminoïd ammonia obtained is actually less than the ammonia known to be present in the test solution.

4. Mr. Wanklyn advises that in estimating the albuminoïd ammonia two or three separate determinations of ammonia should be made. Three separate quantities of 50 c.c. each are to be collected and Nesslerised. The several amounts obtained are then to be added together, and finally the total is to be multiplied by 2, in order to bring the results into parts per million.

It will scarcely be disputed that the eye can only detect shades of colour within a certain range. I believe that twelve shades of the peculiar brown produced when the Nessler test is added to an ammonia solution (that is, of course, taking the usual bulk of fluid operated upon) is about the very utmost of our optical power, even in the case of eyes educated in observing tints. But eyes are not equally, nay very far from equally, sensitive in observing and in classifying tints, the fact being that every one is more or less colour-blind. I have been particularly struck with this fact of late, in examining a large number of men on the part of one of the railway companies respecting their colour-sight. It has, I have found, varied surprisingly, although not perhaps to the same extent as their hearing power. Limiting myself for the moment, however, to one point (for I purpose detailing the results of my experiments on these matters in another place), I tried every man with a series of brown solutions, in fact with the

Nessler test-solutions, and I found that in at least 60 per cent. they failed to arrange the bottles in the proper order of their tints. I very much doubt, therefore, whether two men are likely to judge alike the exact tint-depth of a solution. I doubt, moreover, if tint-depth can ever be made an accurate quantitative measure, but at any rate I am positive that in every experiment it is right to assume a certain error of observation, which error, unfortunately, is not a constant, but varies with different eyes. But according to Mr. Wanklyn's method of analysis it is not *one* error of observation that occurs, but *three* errors of observation (for it is directed that the ammonia in three or four portions of distillate is to be estimated), and not three or four errors of observation merely, but *three or four errors multiplied by* 2, in order that this albuminoïd ammonia, for reasons I am totally at a loss to understand, may be expressed in parts per million. Here, then, is a source of enormous error. No wonder that one person gets one result and one another. And this error is serious; because it must be remarked that in drawing our conclusions from the analysis, a very small difference in the quantity of albuminoïd ammonia (in fact a difference between 0·05 part per million and 0·1 per million) decides us whether we report a water as of "extraordinary organic purity," that is, exceptionally pure and wholesome, or, to use Mr. Wanklyn's phrase, "dirty," that is, I presume, contaminated and unwholesome. With this enormous issue before us, are the difficulties of colour-sight and errors of observation multiplied 6 and 8 fold to be ignored?

5. Again, it must be borne in mind (and I think the circumstance is too often overlooked) that in determining the potability or non-potability of a water, Mr. Wanklyn regards the free ammonia as an important factor in addition to the albuminoïd ammonia. *Per se*, he regards its indication as important, but he would seem to regard its quantitative relationship to the albuminoïd ammonia as of very considerable importance.

Now I am convinced that it is possible to place a very false and a very exaggerated importance on the free ammonia present in a water as a proof of unwholesomeness, and an equally exaggerated importance on its absence as a proof of wholesomeness. Its *presence* within certain limits means and matters, in my experience, very little. For consider what very slight causes will impart ammonia to a water. To mention only one, a few particles of soot from a chimney are quite sufficient to impart definite traces of ammonia to a water otherwise entirely free from it. Nor does its *absence* imply much. We know how unstable a body ammonia is, and the rapidity with which it disappears, affording by no remnant any clue to the past. So far as free ammonia is concerned, I have certainly come to the conclusion that within certain limits its presence or its absence are indications of very little real value,

and in no way affect the wholesomeness or unwholesomeness of the water.

Mr. Wanklyn, however, in his ammonia process, as already observed, regards this free ammonia as a factor of grave importance. For instance, he says that although the albuminoïd ammonia may reach 0·1 part per million—that is, may reach the point where "the dirty-water" class begins, nevertheless the water is not to be actually condemned if the quantity of free ammonia be very small. And again, given a quantity of free ammonia exceeding 0·08 part per million, Mr. Wanklyn would condemn the water at once because he regards such a quantity as evidence that the water is dilute urine in a recent condition. Moreover that, if a water contains a quantity equal to, or exceeding 0·08 part of ammonia per million (that is, 0·0056 grain per gallon), he regards the ammonia as invariably proceeding from the fermentation of urea. I can scarcely think that Mr. Wanklyn is serious in this statement: but allowing that he is so, my own experience is absolutely at variance with his.

Having now dealt with the ammonia process in detail and as a whole, I should wish to state my belief, as the result of by no means a limited experience, that the ammonia process gives fairly concordant results when uniformly conducted; by that I mean given solutions made by the same person—given the same hands to manipulate—given the same eyes to judge the tint-depths. But this is almost of itself a fatal objection to its general employment in water analysis. For it follows, if what I say be true, that in the ammonia process every man must be a law unto himself, whilst one man's law is no one else's law. Hence comparisons are rendered impossible.

Again, I have no doubt that the albuminoïd ammonia process, as a rule, enables you to say whether a water be of excellent quality. It may, moreover, enable you to say if a water be exceptionally bad, although in this respect it may fail, for a peaty water yields a flood of albuminoïd ammonia, and I know of no evidence (whatever may be said to the contrary) to show that a peaty water is unwholesome. But in those more delicate and difficult cases, where a water is not what we may term excellent, but nevertheless is not "dirty," I am of opinion that the ammonia process absolutely and entirely fails.

Let me give you an illustration of strange results obtained by the ammonia process, and also of yet more strangely curious conclusions drawn from them. During last parliamentary session a certain water question was before a Committee on which, as usual, several chemists were called on both sides. On the one side there were those who contended that the water in question was unfit to drink; and a very able chemist, known to most of us, supported this view of the case. The only estimation of the organic impurity of the water that he put

in evidence was the quantity of albuminoïd ammonia yielded by the water. It was, however, pointed out to him in cross-examination that the quantity of albuminoïd ammonia (viz., 0·02 part per million) that he found in the water, which in examination in chief he had termed "horribly polluted," would, according to the learned inventor of the process, class the water as one of extraordinary organic purity. He admitted most frankly that this was so, and, moreover, stated that he was himself astonished at the small quantity of albuminoïd ammonia the water yielded, an astonishment, I confess, in which I quite shared, seeing that the water in question was a river water. His results and conclusions scarcely agreed. By the results the water was proved to be of great, nay of extraordinary, purity; but the conclusion the professor drew from the analysis was, that the water was bad and unfit to drink.

(*b.*) *The Oxygen Process.*

I turn now to the process which I will call, for sake of distinction, "*the oxyyen process.*"

Every chemist knows that when substances capable of combining with oxygen are acted on by a solution of potassic permanganate in water, the potassic permanganate effects their oxidation at the expense of a part of its own oxygen. Let me take oxalic acid as an illustration of what I mean. To a solution containing 8 grains of oxalic acid (acidulated with sulphuric acid) an excess of potassic permanganate is added. It will be found that the 8 grains of oxalic acid will use up exactly 1 grain of the available oxygen of the potassic permanganate (the latter being converted into manganic sulphate), whereby the complete oxidation of the oxalic acid into carbonic anhydride and water will be effected.

And here let me remark, that I merely quote the case of oxalic acid as a convenient illustration.

Before I describe what I consider the best method of determining the oxygen required to oxidise the organic and other oxidisable matters in a water, I shall be excused remarking that there is a wrong way of making the experiment, and that the wrong way is the one commonly described and adopted. I cannot help thinking that even Dr. Frankland's strictures on the process may have been the result of some such imperfections of experiment. I will read you in justification of this remark, Mr. Wanklyn's account of the process from the fourth edition of his book on water analysis. I am of course aware that this work is especially devoted to the description of the ammonia process, nevertheless I think it would have been better to have

described more accurately the method of performing the experiment with potassic permanganate, in order to allow others to judge of its merits and of its defects:

"The next process which was tried was" (says Mr. Wanklyn) "the permanganate process. A dilute solution of permanganate of potash of ascertained strength was prepared. To a given volume of the water to be tested, this standard solution of permanganate was added as long as it was decolorised by the water. From the quantity of permanganate destroyed, the quantity of oxygen taken up by the water could be calculated, and waters could be compared together as to their deoxidising powers."

I am free to admit that, conducted in this way, the permanganate process is irregular, inaccurate, and wanting in delicacy.

The use of potassic permanganate in water analysis was suggested by Professor Forchhammer, of Copenhagen, in 1850. It was afterwards further tried and approved by Condy, Dr. Miller, and Dr. Woods. Dr. Letheby afterwards devoted a great deal of time to it, and the process I now lay before you was the one adopted by him, and was, I believe, in the main suggested by Mr. Harcourt. Nothing was left untried by Dr. Letheby to give accuracy to the results by the oxygen test, and any little that I may have done since in increasing the accuracy of its indications must be accounted for by the circumstance that I have been enabled to take up the work exactly where he left it, without re-treading an inch of the ground which he so laboriously trod.

I will now proceed to describe the process exactly as it should be performed. As I am in the habit (and have been all my life) of working by septems (every septem being equivalent to 7 grains or the $\frac{1}{10,000}$th part of a gallon of distilled water at standard temperature) I shall adopt this in my description of the process.

The following are the solutions required, and the strengths of the solutions found most convenient:—

1. *Dilute Sulphuric Acid.*—1 part of pure sulphuric acid with 3 parts of distilled water.

2. *Solution of Potassic Permanganate.*—2 grains in 1,000 septems ($\frac{1}{10}$th of a gallon) of water. (20 septems, or 0·04 grains of potassic permanganate, contain 0·010 of available oxygen).

3. *Potassic Iodide Solution.*—1 part of potassic iodide in 10 of water.

4. *Sodic Hyposulphite* ($Na_2S_2O_3$) *Solution.*—5·4 grains in 1,000 septems (or $\frac{1}{10}$th of a gallon) of water.

5. *Starch Solution.*—10 grains of starch to be rubbed up with 100

septems of boiling water and filtered. The filtered liquid is then boiled and afterwards allowed to stand for 24 hours, after which the clear solution is syphoned off.

Two glass flasks, each of about 20-ozs. capacity, must be carefully cleansed by rinsing them out first with strong sulphuric acid and afterwards with water under a running tap.

Into each flask is placed 500 septems (that is the $\frac{1}{20}$th part of a gallon) of the water to be examined. We now add to the water contained in each flask from a pipette 20 septems of the dilute sulphuric acid and afterwards 20 septems of the permanganate solution, noting the exact time at which the permanganate solution was added. In 99 cases out of 100 the oxygen contained in 20 septems of the permanganate solution of the strength indicated, will be sufficient to oxidise everything in the water capable of oxidation. If, however, it proves insufficient (which must be judged by the entire disappearance of the pink tint within the prescribed time), a second and, if needful, a third or fourth dose of the permanganate solution (each dose consisting of 20 septems) must be added until the colour remains permanent, proving that an excess of the permanganate has been used. The exact quantity of the permanganate solution added must be noted.

It will be convenient to note here the reaction which occurs when the potassic permanganate is added to the solution of dilute sulphuric acid—

$$Mn_2O_8K_2 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O.$$

From this it is evident that every molecule of potassic permanganate liberates 5 atoms of oxygen, or, in other words, that every 316 parts by weight of potassic permanganate contains 80 parts by weight of available oxygen.

Further, it is evident that the solution of potassic permanganate of the strength recommended for the experiment (viz., 2 grains in 1,000 septems) contains—

0·506	grain	of	available	oxygen	in	1,000	septems of the solution.
0·0506	,,	,,	,,	100	,,	,,	,,
0·00506	,,	,,	,,	10	,,	,,	,,
0·01012	,,	,,	,,	20	,,	,,	,,

It may be taken therefore that every 20 septems of the solution contains 0·01 grain of available oxygen.

The oxygen used up by the constituents of the water is to be estimated in one of the flasks at the end of one hour, and in the other flask at the end of three hours. This is conveniently effected as follows:—

Two drops of the potassic iodide solution are first of all added to the water when iodine is liberated from the potassic iodide, the quantity so liberated being directly dependent on the quantity of potassic permanganate remaining in the water undecomposed. The following may be taken to be the reaction that occurs:—

$$Mn_2O_8K_2 + 10KI + 8H_2SO_4 = 2MnSO_4 + 6K_2SO_4 + 8H_2O + 5I_2.$$

It is evident therefore that 1 molecule, or 316 parts by weight, of potassic permanganate, liberates 10 atoms, or 1,270 parts by weight of iodine from potassic iodide, our previous equation proving that the 1 molecule of potassic permanganate was equivalent to 5 atoms, or to 80 parts by weight, of available oxygen.

Our next question therefore is, How much iodine has been liberated by the potassic permanganate remaining in the water undecomposed? This is determined by the standard solution of sodic hyposulphite (thiosulphate, $Na_2S_2O_3$).

The exact value of the sodic hyposulphite solution must be determined afresh with each experiment, on account of the changes the salt in solution undergoes. To this end proceed as follows:—

A blank experiment with distilled water, in all respects similar to the actual experiment, is first made. 500 septems of distilled water must be put into a perfectly clean flask, to which 20 septems of the dilute acid and 20 septems of the potassic permanganate solution are to be added. This must be done along with the actual experiment, and in like manner the distilled waters must be allowed to remain for one and for three hours. To the water the potassic iodide is now added, and the amount of iodine liberated determined by the solution of sodic hyposulphite. This is done by adding the solution septem by septem from a burette until the yellow colour of the iodine *very nearly* disappears. A few drops of clear starch water are now added, and the hyposulphite solution again dropped in from the burette until the exact spot is reached where the blue colour of the starch iodide disappears. That the exact mark has not been overshot must be proved by the addition of a drop of the permanganate solution, which, by liberating fresh iodine, immediately restores the colour. A similar return of colour moreover should occur after the water experimented upon has been exposed to the air for about five minutes. The number of septems of the hyposulphite solution is now to be read off and noted.

The reaction of the hyposulphite solution on the free iodine is expressed by the following equation, which shows the formation of sodic iodide and sodic tetrathionate:—

$$2S_2Na_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

As we have already shown that 316 parts by weight of potassic per-

University of Michigan

manganate liberate 1,270 parts by weight of iodine, or that 2 grains of permanganate liberate 8·038 grains of iodine from potassic iodide, the number of septems of the hyposulphite solution required will be equivalent to 0·16076 grain of iodine or to 0·0101 of oxygen.

We now proceed in exactly a similar way to determine the number of septems of our standardised hyposulphite solution that is required to combine with the iodine liberated by the potassic permanganate that remains undecomposed in the water under examination; that is, we first add a few drops of the potassic iodide solution and then the standard hypo-solution, determining the exact spot where the free iodine has been satisfied as before, viz., by the addition towards the end of the experiment of a few drops of the starch solution.

It has been suggested by several, especially by M. Monnier (*Compt. rend.*), to heat the water to 70° C. after the permanganate is added. I have made a large number of experiments in this direction, and without stating details, I have arrived at the general conclusion that far more accurate and constant results are obtained by operating at the ordinary temperature of the day, any variation in which is compensated for by a similar action in the experiment made with distilled water, and which is employed on every occasion of conducting the test.

The process as stated may appear somewhat complicated, but in practice is remarkably easy.

Let me simply and without details repeat the method of making the examination, and give at the same time the results of an actual experiment in order to demonstrate the working.

Into two clean flasks place 500 septems of the water; add to each 20 septems of dilute sulphuric acid and 20 septems of the permanganate solution.

Note the exact time at which the permanganate solution was added.

At the same time two similar quantities of distilled water are to be treated in a precisely similar manner. [It is evident that any number of waters may be put on at the same time, one set only of the distilled water series being sufficient for any number of waters.]

At the end of one hour and at the end of three hours the oxygen used up by the water is to be determined. To one flask of the distilled water add a sufficiency of potassic iodide and then the hyposulphite solution from a burette until the whole of the free iodine is removed, judging this exact spot by the addition towards the end of the experiment of a few drops of the starch solution.

Read off the number of septems added.

An experiment exactly similar in every respect is to be made with

the water we are examining, and the number of septems added are to be noted.

Experiment. Say 20 septems of potassic permanganate have been added in each case:—

At the end of one hour—

Septems of hyposulphite solution required to combine with the free iodine in the distilled water 50
Septems of hyposulphite solution required to combine with the free iodine in the water under examination..... 40

At the end of three hours—

Septems of hyposulphite solution required to combine with the free iodine in distilled water 50
Septems of hyposulphite solution required to combine with the free iodine in water under examination 30

From these we deduce the oxygen required by the water.

In each case 50 septems of the hyposulphite solution were used in the blank experiment.

Therefore 50 septems are equivalent to 0·01 of oxygen
" " " 0·1607 of iodine.

This constitutes therefore the value of the hypo-solution.

After one hour in the water under examination only 40 septems were required. The quantity of oxygen used therefore may be found as follows:—

(α.) 50 : 40 :: 0·01 : x (= 0·008.)

(β.) 0·01 − 0·008 = 0·002 quantity of oxygen required to oxidise the organic and other matters in 500 septems of water.

(γ.) 0·002 × 20 = 0·04 oxygen required to oxidise organic matters, &c., in 10,000 septems or one gallon of water.

In a similar manner the oxygen used after three hours may be estimated.

The working may be rendered less complicated as follows:—

Let X = number of septems of hypo used in the distilled water.
" Y = number of septems used in the water under examination.

If 20 septems of the permanganate solution have been used:—

Then $\frac{X - Y \times 0{\cdot}20}{X}$ = oxygen required to oxidise organic matters, in one gallon of the water.

If 40 septems of permanganate had been added the formula would be as follows:—

$$\frac{X \times 2 - Y \times 0{\cdot}20}{X} = \text{oxygen required by one gallon.}$$

If 60 septems had been added, then as follows:—

$$\frac{X \times 3 - Y \times 0{\cdot}20}{X} = \text{oxygen required by one gallon;}$$

and so on.

We shall thus be able to state from our experiments the oxygen used by the water at the end of one hour and of three hours, which in the illustration in question is as follows:—

1. Oxygen required by one gallon of the water after one hour ..... 0·040 grain
2. Oxygen required by one gallon of the water after three hours ..... 0·080 „

We have next to enquire how far the oxygen process is influenced, and the results interfered with, by the presence of the various inorganic constituents common to drinking water.

As regards the earthy carbonates and sulphates, experiments with weak and saturated solutions of these salts prove that they are absolutely without action on potassic permanganate.

In the following table I have given the results of some experiments with sodic, calcic, and magnesic chlorides. The East London Company's water was used in all these experiments, partly because it was at hand, and partly because it was a water with the composition of which I was familiar.

Experiments illustrating the influence of the Alkaline and Earthy Chlorides on the Oxygen test.

	Sodic Chloride.	Oxygen required to oxidise organic and other matters per gallon.
East London water		0·041
„ „	+ 10 grains sodic chloride per gallon	0·041
„ „	+ 20 „ „	0·041
„ „	+ 30 „ „	0·042
„ „	+ 40 „ „	0·041
„ „	+ 50 „ „	0·042
„ „	+100 „ „	0·042
„ „	+150 „ „	0·042
„ „	+300 „ „	0·043
„ „	+400 „ „	0·043

	Calcic Chloride.	Oxygen required to oxidise organic and other matters, per gallon.
East London water	.....	0·041
„ „	+ 20 grains calcic chloride per gallon	0·044
„ „	+ 40 „ „	0·048
„ „	+ 60 „ „	0·051
„ „	+ 80 „ „	0·054
	Magnesic Chloride.	
East London water	.....	0·055
„ „	+ 10 gr. magnesic chloride per gallon	0·058
„ „	+ 20 „ „	0·061
„ „	+ 40 „ „	0·068

This table shows that sodic chloride is practically without influence on the oxygen test, although the salt was added in several cases in very large quantity: that is to say, the ordinary East London Company's water required on the day the experiment was made 0·041 grain of oxygen to oxidise its oxidisable constituents, whilst 0·043 grain of oxygen (that is a difference merely of 0·002 of a grain) was needed when 400 grains per gallon of common salt had been added to the water.

In the case, however, of calcic and magnesic chlorides, a slight influence is to be remarked, the increase of oxygen in both cases being tolerably uniform for given quantities of the salts added.

In the following table I have given the results of numerous experiments conducted in a similar manner with the East London Company's water, to which known quantities of potassic, calcic, and magnesic nitrates had been added:—

Experiments illustrating the influence of certain Alkaline and Earthy Nitrates on the Oxygen tests.

	Potassic Nitrate.	Oxygen required to oxidise organic matters, &c., per gallon.
East London water	.....	0·049
„ „	+ 5 grains of potassic nitrate per gallon	0·049
„ „	+10 „ „	0·049
„ „	+20 „ „	0·050
„ „	+40 „ „	0·049
	Magnesic Nitrate.	
East London water	.....	0·043
„ „	+10 grains of magnesic nitrate per gallon	0·044
„ „	+40 „ „	0·048

	Calcic Nitrate.	Oxygen required to oxidise organic matters, &c., per gallon.
East London water		0·043
„ „	+10 grains of calcic nitrate per gallon	0·046
„ „	+20 „ „	0·047
„ „	+40 „ „	0·050

Again I would note that the alkaline nitrates appear to exercise no influence on the experiment, but that a slight, although a tolerably uniform action is noticeable in the case of the nitrates of lime and magnesia. I have thought it advisable to place these experiments before you, at the same time that I think for all practical purposes, considering the very slight influence of the calcic and magnesic nitrates, even when added in enormous quantities—quantities far beyond what we are accustomed to find in ordinary waters, we may be content to ignore their presence in our calculations.

The case, however, is different with certain other mineral constituents. But their number is, after all, very limited, viz., ferrous salts (and other metallic proto salts), sulphuretted hydrogen, and nitrites.

As regards *iron*, its action on the permanganate is admittedly very marked. But the presence of iron could scarcely be overlooked in the course of a water analysis, if present in anything approaching appreciable quantity. Having determined the amount of iron in the water, its extent of influence is easily estimated.

And here let me note that there are certain observations to be made of the greatest possible importance, before commencing a detailed investigation of a water. The *taste* of a water, so far as iron is concerned, is a valuable point to record; beyond this, however (excepting, perhaps, the slight bitterness of peat), I have but little faith in the value attached by some to water palatability or non-palatability. Unfortunately the best-tasted waters are often seriously suspicious (for nitrates and chlorides are singularly powerful in exciting the action of the salivary glands), whilst an unpleasantly tasted water is often the opposite to impure. If a water be suspected of containing iron, the 2-foot tube serves as a valuable instrument. Fill three tubes with the water; into one place a drop or two of a solution of ammonic sulphocyanide; to the second add first of all a few drops of nitric acid, and then a few drops of the ammonic sulphocyanide solution, and compare the tint depths of these tubes one with the other, and of both with the pure water tube. Very valuable evidence will in this way be gained as to the presence of iron, and the form in which it is present.

It can scarcely, I should think, be possible to overlook the existence of *sulphuretted hydrogen* in a water. The *odour* evolved by a water should in every case be noted. The best method of testing this is to

half fill a quart stoppered wide-mouthed bottle with the water, tie down the stopper, and place the bottle in a warm place. At the end of an hour or so remove the stopper, and take a good sniff at the contents. A very exaggerated importance has, however, been assigned to the odour, as well as to the taste, of waters. For instance, a modern treatise remarks that by the odour you can distinguish river from spring water. Taste and odour are both to be regarded, undoubtedly, but we must be careful to regard the evidence of smell and taste at their proper, and not at their improper, value. I cannot think sulphuretted hydrogen can be fairly deemed a difficulty to the oxygen test.

With respect to *nitrites*, however, the case is far different, for they cannot be detected by the taste like iron, nor by the smell like sulphuretted hydrogen. They, moreover, to use Dr. Frankland's words, "surpass every form of organic matter experimented upon in the avidity with which they absorb oxygen." Granted that this is so. Dr. Frankland, however, adds, "Thus it is evident that for the estimation of the amount of organic matter in water, or the quantity of oxygen necessary to oxidise that organic matter, permanganate of potash is utterly untrustworthy." But why so? We know the power of nitrites on permanganate. They are no unknown rocks in water analysis. All, therefore, we have to do is to eliminate the error resulting from their presence, by estimating the quantity of nitrites present, which may be done by determining the oxygen required within such period, that whilst the oxidation of the nitrites shall be complete, the oxidation of the organic matter shall not have commenced. And this is perfectly practicable. Before, therefore, commencing the determination of the organic matter by the oxygen process, first of all (*i.e.*, preparatory to a more accurate experiment) determine the presence or the absence of nitrites by dropping into a few ounces of the water a sufficient quantity of the permanganate solution to impart to the water a perceptibly pink tinge. If on standing for two or three minutes there is a manifest loss of colour, the presence of nitrites is indicated, whilst on the contrary, if the colour be persistent, their absence from the water may be concluded. If nitrites are present, the quantity may be easily enough estimated by adding to a given quantity of the acidulated water a known quantity of the permanganate solution, taking care the solution is in excess, and estimating the oxygen absorbed, after standing three minutes in the ordinary manner, within which time all nitrites will be oxidised, whilst the organic matter will remain unchanged.

But such an experimental determination of the nitrites is rarely required, for nitrites are not very common ingredients of ordinary waters. My own experience (and I have examined hundreds of waters to determine this point) does not coincide with that of Dr. Frankland,

when he speaks of them as of frequent occurrence in potable waters. They are occasionally present, I admit, but that they are frequently present, I dispute. But suppose they are present, surely their presence is a bad indication. The only charge, therefore, to be brought on this score against the oxygen process is that it records their presence (admittedly an evil, for their presence indicates organic matter of very recent oxidation) conjointly with the organic impurity—that is, provided a separate estimation of the nitrite be not made, and which I contend, is easily done. The fact that the oxygen process takes cognisance of the nitrites is, in my opinion, an argument in its favour.

Of course the oxygen test, like every other chemical test, must be used with intelligence.

But admit that other things reduce the permanganate besides organic matter. What then? Why it simply exaggerates your results. Admit iron, admit sulphuretted hydrogen, admit nitrites to be fallacies, we ask, in what direction are they fallacies? They may be fallacies in leading us to regard a water as worse than what it is, but never as better than what it is. There is no evidence that deleterious substances may be present in water which are not accounted for by the permanganate. And there is all the difference to the sanitarian between condemning a water that is harmless, and approving a water that is dangerous. So far as I know, no one has ever brought the latter charge against the oxygen test. If nitrites, if iron, if sulphuretted hydrogen be present (and these constitute the difficulties), they are certain to be detected if the water analysis be properly conducted, and if they are not detected, if present, I should regard the analyst's determination of the organic matter as of very little value.

Are all organic substances equally affected by the action of potassic permanganate? This is our next question. I answer, Certainly not. Dr. Frankland referred to this as an objection to the oxygen process in his paper read before the Chemical Society in 1868, and exhibited a table in illustration of the objection, which I here reproduce in part:—

Name of substance, 3 parts of which were carbonised in 100,000 parts of water.	Oxygen absorbed in 10 minutes.	Oxygen absorbed in 6 hours.
Gum arabic	0·0102	0·0350
Cane sugar	0·0064	0·0152
Starch	0·0143	0·0302
Gelatin	0·0792	0·1836
Creatine	0·0080	0·0172
Alcohol	0·0093	0·0164
Urea	0·0092	0·0119
Hippuric acid	0·0328	0·0600

That, however, organic bodies were not equally affected by the permanganate I have been fully aware ever since I commenced working the process. Take, for example, white sugar. On June 17th I made a solution of white sugar, containing 2 grains in 1,000 septems of distilled water. I tested this solution on 18 different occasions, from and including June 17th to October 2nd (1875). The results show conclusively that the crystallised sugar is not easily attacked by the oxygen of the permanganate, and further that the sugar itself seemed to undergo little or no change in solution. The following are the results :—

Date.	Septems of permanganate solution used.	Value of hyposulphite solution in septems.	Hyposulphite solution (in septems) required	
			in distilled water containing 20 septems (0·04 grain) of the solution of sugar.	in distilled water containing 40 septems (0·08 grain) of the solution of sugar.
June 17	20	52	52	50
19	,,	53	53	53
21	,,	52	51	51
24	,,	49	47	46
28	,,	53	51	51
July 1	,,	52	51	50
4	,,	53	51	50
8	,,	57	54	53
12	,,	54	52	52
15	,,	53	52	52
August 9	,,	51	50	49
17	,,	53	50	50
23	,,	57	54	53
31	,,	54	52	52
Sept. 9	,,	54	52	51
18	,,	51	50	49
25	,,	50	49	47
October 2	,,	55	54	53
Total	360	953	925	912

In the following table I give the results of experiments on a series of bodies of organic origin—using first of all a fresh solution of the various substances, and estimating the oxygen required by it after standing for one and three hours, and afterwards using a solution which had been allowed to stand for 48 hours, and estimating the oxygen required in a similar manner after acting for similar times :—

Action of Potassic Permanganate on various Bodies at various Times.

[In each case the strength of the Substance operated upon was 3 grains to 1 gallon of Water.]

	Fresh solution.		Solution after being kept for 48 hours.	
	Oxygen used per gallon during 1 hour.	Oxygen used per gallon during 3 hours.	Oxygen used per gallon during 1 hour.	Oxygen used per gallon during 3 hours.
	grain.	grain.	grain.	grain.
Gum	0·003	0·007	0·003	0·009
Gelatine	0·014	0·021	0·014	0·035
Hippuric acid	0·042	0·046	0·041	0·045
Sugar	0·000	0·003	0·000	0·009
Morphia	1·307	1·450	1·248	1·406
Strychnia	0·528	0·775	0·496	0·703
Starch	0·014	0·014	0·000	0·003
Urea	0·000	0·000	0·000	0·000
Uric acid	0·189	0·282	0·209	0·283

This table shows that there are many substances of organic origin which appear to be almost as inert as cane sugar on potassic permanganate. The point, however, we have set ourselves to determine in a water analysis is the wholesomeness or unwholesomeness of a water submitted to us, and of course the question we naturally ask is, what is the harm of cane sugar or starch or gum and bodies resembling them so far as the non-reduction of permanganate is concerned, even if they are present? Admitting, as I am willing to do, that the oxygen process cannot be used with scientific precision for the purpose of estimating the actual quantity of organic matter in a water, inasmuch as there are many substances (most of which are crystalline) that are altogether unacted upon, or very slowly acted upon, by the oxygen of permanganate, nevertheless I claim for the oxygen process in water analysis that the bare statement of the oxygen used to oxidise the organic and other oxidisable matters affords the most positive evidence (evidence to my mind beyond dispute) of the relative quantity of matters in the water likely to be injurious (for it is the offensive and deleterious we wish to hunt out, and not the inert and the harmless), and enables us to speak with confidence in advising the use of, or the rejection of, a water for drinking purposes. This is all that is wanted. For water analysis is unlike a commercial analysis where every unit means money.

It is not unlikely that I shall be reminded that in my monthly reports on the Metropolitan waters, a note appears stating that the quantity of the organic matter in the water is about eight times the

amount of oxygen required by it. I have allowed this note to remain since I have reported on these waters to the Society of Medical Officers of Health, and must, of course, take the responsibility of having done so; nevertheless, I may venture to remark that I was not the author of it, and that this month I have erased the note from my report. In the case of the London waters, however, I think I have abundant experiments to prove that the oxygen used multiplied by 8 denotes very nearly the actual quantity of organic matter present, nor would it be difficult to obtain further evidence (if it were required) on this point from the work of others. That the estimation of the organic matter by such a calculation is of universal application, however, would, I admit, be a false conclusion, and one that facts do not justify. Except in a few cases therefore in which I distinctly state the method adopted in making the estimation, I have discontinued giving the quantity of organic matter calculated on this supposition. I am anxious not to be misunderstood on this point, and therefore briefly to repeat what I have said, I am of opinion that in the case of certain waters the quantity of organic matter is closely represented by multiplying the oxygen used up by the water during three hours by 8, but that we are not justified in assuming that such an estimation necessarily applies to all waters, and that therefore, having regard to scientific precision, it is advisable, in reporting on waters by the oxygen process, to state merely the quantity of oxygen required by the water, the determination of which is absolutely certain, rather than the quantity of organic matter estimated from the oxygen, the determination of which at best is uncertain.

I now consider a question of great importance. Say we have determined the oxygen required by the oxidisable constituents of the water by a solution of potassic permanganate acting for three hours. We have further, if nitrites are present, eliminated the error they would occasion. We have now obtained a statement of the oxygen required to oxidise the organic matter (and probably that only) in the water. Can we by any modifications of the oxygen process itself, or by any further observations, obtain more definite information as to *the kind of organic matter* effecting this reduction of the permanganate? I think it is possible to do so in two ways:—

First. By comparing together the oxygen used during the first hour the permanganate is allowed to act, with that used during the second and third hours.

Secondly. By an examination of the tint and tint-depth of the water as seen in bulk, as *e.g.*, in a 2-foot tube.

I. With respect to the first of these points, viz., a comparison of the oxygen used in the first hour with that used in the second and third

hours, I am daily more and more convinced that we obtain by this means data of great value by which to judge the nature of the organic impurity. Without stating definitely that I should be justified in expressing numerically the ratio of animal to vegetable matter by this means, I am not without hopes that I shall be able to do so before long with substantial accuracy. At any rate it undoubtedly furnishes us with exact information as to the relative quantities of putrescent and easily oxidisable matter, and of non-putrescent or less easily oxidisable matters, present in the water. The former (viz., the putrescent organic matters) it indicates quantitatively with great accuracy; the latter (viz., the non-putrescent matters) are scarcely capable of the same exact estimation as the former, for they are bodies for the most part of difficult oxidation. But this is really a matter of secondary consequence: for (and here I am happy to quote Dr. Frankland's own words) "The most pernicious organic matters" (that is, I suppose, putrescent organic matters) "are those most easily oxidised by potassic permanganate" (*Chemical News*, March 23rd, 1860, p. 136). I do not propose just now troubling you with a series of experiments I have conducted, and am conducting, on the action of the permanganate on putrescent and non-putrescent, and on animal and vegetable, organic matter; but I content myself at this point with referring you to the two following tables, illustrating in Table I the action of potassic permanganate on urine diluted with water, and in Table II its action on a mixture of urine and apple-juice in distilled water. I had hoped, in estimating the oxygen required during the first hour, to have abandoned the use of the dilute acid. In this I have not been so successful as I could have wished, but I still hope to accomplish what I think will render the line dividing putrescent from non-putrescent organic matter sharper and better defined:—

TABLE I.—*Oxygen required to oxidise Mixtures of Urine and Distilled Water after standing various times.*

	Oxygen used per gallon during 1 hour.	Oxygen used per gallon during 2 hours.	Oxygen used per gallon during 3 hours.	Oxygen used per gallon during 4 hours.
	grain.	grain.	grain.	grain.
20 septems of urine in 10,000 septems of water (1 in 500).	0·061	0·061	0·072	0·076
40 septems of urine in 10,000 septems of water (1 in 250).	0·118	0·120	0·141	0·149
60 septems of urine in 10,000 septems of water (1 in 167).	0·181	0·181	0·189	0·194

TABLE II.—*Oxygen required to oxidise Mixtures of the same Urine employed in Table I with distilled Water, to which some Apple Juice had been added* (2*oz.* to 1 *gallon*).

	Oxygen used per gallon during 1 hour.	Oxygen used per gallon during 2 hours.	Oxygen used per gallon during 3 hours.	Oxygen used per gallon during 4 hours.
	grain.	grain.	grain.	grain
20 septems of urine in 10,000 septems of mixture of water and apple-juice.	0·063	0·065	0·112	0·135
40 septems of urine in 10,000 septems of mixture of water and apple-juice.	0·121	0·129	0·204	0·234
60 septems of urine in 10,000 septems of mixture of water and apple-juice.	0·190	0·199	0·258	0·285

I should wish to draw your attention to one or two points in these tables.

First. I would remark on the general relationship of the results in Table I.

Thus, when 40 septems of urine were employed in the experiment, the oxygen required was as nearly as possible double at all periods that used when only 20 septems of the urine had been added, whilst it was in each experiment treble when 60 septems were added, the error in no case extending beyond the third place of decimals.

Secondly. It is to be remarked that the oxidation of whatever matters are capable of oxidation by potassic permanganate in urine is nearly complete within the first hour—that between the first and second hours there is a lull in the process, no oxidation practically going on—that after the second hour, oxidation, although to a limited extent, begins again. What the various substances are which reduce the permanganate during the first hour, and what between the second and third hours, I am not going to speculate, but one thing appears to me certain, that considering the definite and not inconsiderable interval that occurs during which oxidation seems to be suspended, we are justified in concluding that the substance or substances that reduce the permanganate in the first hour, are different from the substances that reduce the permanganate in the third hour. Be this as it may, the important fact remains that the oxidation of what-

ever is present in urine capable of oxidation by potassic permanganate, is nearly complete within one hour.

I have now to draw your attention to the second table, the only difference being that, in addition to the urine, a certain quantity of a vegetable juice, namely, apple-juice, had been added. Again, I remark, the results of the table taken by itself are strictly comparable, 0·063 grain of oxygen being used during the first hour with 20 septems of urine, 0·121 with 40 septems, and 0·190 with 60 septems. Again, there is a certain lull between the first and second hours, but between the second and third hours the oxygen required is considerable.

But now compare Table II with Table I, remembering that the only difference between the solutions experimented upon is that in the latter table some apple-juice had been added to the mixture. And we have these facts before us :—

(1.) That during the first hour the apple-juice made but little difference to the oxygen used up by the water, that is, instead of 0·061 grain of oxygen with 20 septems of urine, 0·063 grain was required, and instead of 0·118 and 0·181 with 40 and 60 septems respectively, 0·121 and 0·190 grain were required.

(2.) During the second hour the difference is not marked, that is, against 0·061, 0·120, and 0·181, we have 0·065, 0·129, and 0·199 respectively.

(3.) But during the third hour the difference becomes very manifest, for against 0·072 we have 0·112, against 0·141 we have 0·204, and against 0·189 we have 0·258.

(4.) That whereas in the fourth hour in the experiments recorded in Table II oxidation was still going on, there was very little action between the third and fourth hours in the experiments recorded in Table I.

I think these experiments (a first instalment of an extensive series I hope soon to publish) prove that the oxidation of the oxidisable matters in the urine is nearly complete within the first hour, whilst the oxidation of the oxidisable constituents of the apple-juice does not begin until after the second hour.

I will say no more on this point now. I am anxious to be more certain of my ground than I feel at present, before I publish more details, but the results, so far as I have gone, are instructive, and, I need not say, suggestive.

It will be impossible for me in the course of this paper to refer to the action of potassic permanganate on individual vegetable substances. With respect to peat, however, its power of deoxidising permanganate is well known, and inasmuch as a peaty water very frequently comes before us, I may, perhaps, refer to some experiments with peat as

having a practical value. I shall point out directly that the tint of water when examined in bulk will at once reveal its presence or its absence, and thus entirely prevent our confounding injurious animal contamination with organic matter of a peaty nature, from the excessive oxygen that may be used up in our chemical examination of a water.

In the water inquiry of 1867, an excellent sample of peat was collected by Dr. Letheby, on the moors, near Sheffield. It was found in five experiments on solutions of different strength, that the average amount of oxygen required to oxidise 1 part of peat was 0·779.

The solution made in 1867 remained in the laboratory, freely exposed to the air for two years. In 1869 the solution, which then appeared of a dark porter tint, gave on analysis as follows:—

Total solid matter per 1,000 septems....	16·13 grains.
By incineration the 16·13 grains gave—	
Organic	15·17 „
Ash	0·96 „

Regarding this organic matter as peat, it was found in numerous experiments on solutions of different strength, that the average amount of oxygen required to oxidise 1 part of the organic matter was 0·422.

In 1875 the solution (which had been standing since 1869 in the laboratory contained in a tall glass, and covered with a glass valve) was again examined. It still appeared of a dark porter tint, and on analysis gave as follows:—

Total solid matter per 1,000 septems....	9·825 grains.
By incineration the 9·825 grains gave—	
Organic	9·075 „
Ash	0·750 „

Again regarding this organic matter as peat, it was found as the result of 14 experiments with different quantities, that the average amount of oxygen required to oxidise 1 part of the organic matter was 0·321.

It appears, therefore (and I content myself with merely recording the facts), that the oxygen required by each part of peat of different ages by the potassic permanganate test was as follows:—

	Oxygen required to oxidise 1 part of the organic matter (peat).
Fresh peat (1867)	0·779
Peat kept two years in solution (1869)	0·422
„ nine „ „ (1875)	0·371

II. Another means of controlling our chemical examination for organic matter is by an examination of the tint and tint-depth of the

water, as seen through a stratum 2 feet in thickness. I say for organic matter, because I am convinced none of the ordinary mineral constituents of a water in any way affect its colour.

The most convenient method of making the experiment is with a glass tube, 2 feet in length and 2 inches in diameter, closed at both ends with white glass caps, which can be unscrewed at pleasure, for the purpose of cleaning out the tube. A small piece of brass tube is inserted into the side of one of the caps, to allow of the expansion of the water in the tube. I am convinced that to obtain satisfactory results a 2-inch tube at least is required. The tube is filled with the water to be examined, and then placed horizontally on the stand, the light, which should be natural and not artificial light, being reflected through the tube by means of a piece of white card.

Apart from this being a convenient, although a severe means of testing the clearness of a water, and also degrees of turbidity, and consequently (in the case of Water Companies that filter their water) of efficient filtration, there are two very important conclusions that the practised eye may draw from the experiment, viz.:—

1. That the peculiar *tint* of the water is an indication of the *kind* of organic matter present; and

2. That the *tint-depth* is an indication of the *quantity* of organic matter in the water.

I have distinctly said that it must be a practised eye to read the indications thus afforded, for determinations of this nature always require a little practice, just as we know the practised microscopist sees at a glance what the novice fails to see, until his attention is called to it.

Again, neither the tint nor the tint-depth is much to be relied upon in a very turbid water. I need scarcely say I advocate this physical examination of the water only as an adjunct to the chemical examination.

I. That the tint of the water in many cases indicates *the kind* of organic matter present will probably be admitted. The peculiar greenish-brown tint of somewhat recent peat, and the olive-brown tint of an older peat are perfectly distinctive colours. Although the oxygen required to oxidise the organic matter of a peaty water would be large if the permanganate were allowed to act upon it for three hours, nevertheless, our physical examination of the water would at once tell us that the organic matter which had used up the oxygen was in great measure of vegetable origin, and therefore harmless, rather than of animal origin, and therefore possibly dangerous. Again, a water exhibiting an absence of colour, or at most, what is a more strictly accurate description, a very slightly blue tint (for I have never seen an absolutely colourless water in the 2-foot tube) will invariably be found

to be a water of remarkable freedom from organic impurity. A distinctly yellow tint, again, is often a suspicious sign. Thus the check exercised by the colour exhibited by the water when seen in bulk is an important check, telling us, if the oxygen required by the water be very large, whether its origin is probably animal or vegetable, and also giving us a rough indication (certainly not to be relied upon by itself, but although rough, no less useful in its proper place) of the character of the water which we are examining.

II. I have said that the tint-depth is an indication of the *quantity* of organic matter present.

Drs. Frankland and Armstrong think otherwise. They say, "The tinctorial power of many colouring matters is so great as to render them distinctly appreciable to the eye when their amount is far too minute to be detected gravimetrically; thus a litre of water distinctly tinted with ink and magenta, contains an amount of either of these colouring matters too small to be appreciated by the most delicate balance. The yellowish or brownish colour of water appears to be of this character, for it may be removed completely by agitation with aluminic hydrate, and yet a considerable amount of organic matter is still left in the water. Thus a sample of water which had been so treated, and exhibited the blue-green tint of distilled water when viewed through a thick stratum, still contained 0·160 part of organic carbon in 100,000 parts. It is therefore evident that no reliance can be placed upon colour as an indication of the amount of organic matter in waters, for although a dark-tinted water probably contains a considerable amount of organic matter, it by no means follows that a colourless water may not contain even a larger proportion. Thus a sample of peaty water, possessing a decided brown tinge, contained but 0·256 part of organic carbon in 100,000 parts, whilst a sample of water from North Wales, which had been in contact with the fine mud of the stamping engines of mines, was perfectly colourless, although it contained no less than 0·544 part of organic carbon in 100,000 parts."

To the various statements in this paragraph I reply—

1. That ink and magenta are bodies of exceptional colouring power; besides which ink and magenta are not common constituents of drinking water. But suppose they were, Dr. Frankland furnishes us with an excellent argument in favour of noting the colour of a water, for he states "that a litre of water may contain an amount of either of these colouring matters" (and if of these, surely of others, too, although, perhaps, in a lesser degree) "too small to be appreciated by the most delicate balance."

2. His experiment with aluminic hydrate is somewhat incomplete in its details. He does not tell us, to begin with, the quantity of organic

carbon present in the water before it was shaken up with the aluminic hydrate, whilst the 0·160 part of organic carbon in 100,000 parts of the water found after it had been so treated—which water exhibited a *blue-green* tint when examined through a thick stratum (? a 2-foot tube), is exactly the colour I should expect from such a quantity of organic matter in such a case, and clearly denotes that the aluminic hydrate had failed in removing the whole of the colour of the water, because it had failed in removing the whole of the organic matter.

3. I have already admitted the great tinctorial power of peat, a colour of a peculiarly distinctive character. That Dr. Frankland should have found that a quantity of peat represented by 0·256 of organic carbon should impart "a decided brown tinge" to the water is exactly what I should have anticipated.

4. In the last case Dr. Frankland refers to, viz., the case of the muddy water from North Wales, which contained 0·544 part of organic carbon in 100,000 parts, and was yet perfectly colourless, I should like to know if the colour was judged in a stratum of 2 feet or not; and further, it is not quite clear whether the analysis was conducted on the turbid water, or on the water after the sediment had been allowed to deposit.

Having now referred to all the objections I can find to the use of the 2-foot tube for the purpose of assisting a chemical examination, I will endeavour to give the results of my own experiments confirmatory of its value.

The sample of peat collected on the moors, near Sheffield, in the water inquiry of 1867 was used for a series of experiments. The tints obtained with varying quantities show how very distinctive the colour and tint-depth are of the quantity of peat present:—

The Colour Imparted to Water by Peat.

Grains of peat per gallon.	Appearance in Quart Bottle.	Appearance in 2-ft. Tube.
0·024	Nothing noticeable.	A bluish-green tint.
0·049	Closely resembled London water.	A greenish tinge, like Thames water.
0·097	Ditto as above; but slightly darker.	An olive-green colour.
0·121	Ditto; slightly darker than last.	Ditto; darker.
0·171	Appearance objectionable.	An olive-yellow colour.
0·219	Visibly peaty.	Peaty colour; very marked.
0·234	Peaty tinge; more marked.	Peaty colour; still more marked.
0·380	Peaty tinge; still more marked.	Strongly peaty.
0·453	Very distinctly peaty.	Water very dark.
1·135	Peaty colour; strongly marked.	Appearance of porter.
2·269	Appearance of French vinegar.	Black.

I need scarcely do more than point out the manifest advantages of the 2-foot tube over the quart bottle, minute shades of colour being so far better seen in the large bulk of water exhibited by the former. But that is not all. Not simply do I contend that the colour of peat is absolutely distinctive, but that a practised eye can give a very fair approximate opinion as to the quantity of peat present by the tint-depth.

Objection, of course, may be made to this by saying that I am judging all peat by reference to this one specimen. This, however, is not so. On five several occasions these experiments have been repeated with five different specimens of peat. I have selected this set partly because I was more familiar with the actual composition of the peaty material used than I was with the other specimens (it being the one on which the other experiments with peat, to which I have already referred, were conducted), but chiefly because it closely exhibits an average of the whole, although the variations, taking all together, were comparatively small, and not more than sufficient to prove a definite uniformity in the experimental results.

Again, it may be urged that a peaty water may be contaminated with other substances, the tint of which would be overpowered by the colour of the peat, whilst the more delicate tints of these substances would be insufficient to produce a perceptible change in the peat-tint. This, I am ready to admit, might be the case, and would undoubtedly constitute an argument against the use of the 2-foot tube taken by itself, but is no argument against its use as an accessory to chemical analysis.

Quoting in substance Dr. Angus Smith's words (*Chemical News*, June 11, 1869), he says, "Coloured water, if the matter be peaty, may be very unpleasant to look at, without being in any way, so far as I have ever heard, injurious to health. Colourless water may be wholesome or unwholesome. It may, for example, contain the juices of plants of a wholesome character. If these juices are fresh they may do no injury. But they will not long remain fresh—they will putrefy. Water containing organic matter ready to putrefy should be avoided." Hence colourless water may be injurious, and coloured water wholesome. All this is perfectly true. But because the 2-foot tube does not show everything, it by no means follows it does not show something.

This much, then, I claim for the colour test, viz., that as a companion to the chemical analysis, its indications are valuable—first, because it gives us a clue to the kind of organic matter present, and, secondly, in certain cases, because it gives us a clue to the quantity present. Let me give one or two illustrations:—

1. A water exhibits a bluish tint, or, say, appears nearly colourless in

University of Michigan

the 2-foot tube. It, moreover, uses up very little oxygen after standing for three hours in contact with permanganate. The freedom of that water from organic impurity may be relied upon as certain.

2. A water exhibits but little colour, or at most a slightly yellow, or a greenish-yellow tint, nevertheless the oxygen required is found to be large. Such a water as a potable water is suspicious.

3. A water exhibits in the 2-foot tube a decided peaty tint. By experiment it is found to need a large quantity of oxygen after standing for three hours. Knowing that peaty matter acts as a reducing agent on permanganate, and our 2-foot tube revealing the colour of peat, the quantity of oxygen required, although far in excess of what was used in the former case where there was an absence of colour in the water, is not to be regarded with the same suspicion, peaty matter not being injurious to health.

This, then, is what I have to say respecting the oxygen process. My own views of its use in water analysis are expressed pretty much in the words of Dr. Angus Smith (*Chemical News*, September 3, 1869, p. 112), "Nothing ever pretends to do in water analysis what the permanganate test does. Those who neglect it leave out the putrid matter or drive it off in boiling."

Such, then, are the processes in common use for estimating the organic purity or impurity of drinking waters, and their advantages and disadvantages as best I know them. We have now to consider the comparative value of these processes as a guide to a correct answer to the question Which shall we adopt? We can imagine the despair of the young student to know what to do. One says the combustion process is alone trustworthy; another, my process is *the* process—nay, more, all processes except the ammonia process are "processes of the past, to be regarded as of mere historic interest."

Let me here make one general observation. In a matter of such vital importance to the public as the quality of the water they are compelled to drink (for in 999 cases out of 1,000 the public have no alternative but to take what is given them), a question, too, not of pounds, shillings, and pence, but of life or death—of disease or health—nothing can justify us in abandoning a process because it is troublesome, and needs time and patience, or in adopting a process because it is short and easy, provided it can be shown that the slower process yields results of greater accuracy than the more rapid one. I therefore discountenance the argument in such a case as water analysis, which recommends a process on the ground that the analysis can be com-

pleted in some incredibly short time. Such an argument might be of force if our object, as chemists, were the degrading one of simply making analyses on which to support testimonials for puff advertisements. When, however, we are called upon to advise on the quality of a water (I would speak for the moment in the double capacity of physician and chemist), the question of time, within certain limits, is not one, I submit, that should enter into our calculations. The sole question we have to consider is, which process gives the most accurate results on which to decide the wholesomeness or the unwholesomeness of the water submitted to us?

Let me now attempt something like a comparison drawn from a large body of results of the ammonia process and the other two processes described as "of *mere historic interest—processes of the past.*"

It is well known that Dr. Frankland has for some years past examined (by request of the Registrar-General) monthly samples of the water supplied to the Metropolis by the eight London companies entrusted with that duty. He has, of course, adopted the combustion process as the measure of the organic purity of the waters. Similar monthly samples were also examined by Dr. Letheby during his lifetime, and since his death by myself, at the request of the Society of Medical Officers of Health, the oxygen process having been used by both of us as a measure of organic purity, the albuminoïd ammonia having also been estimated at the same time. We have thus a series of experiments allowing of comparison on a large scale. These analyses have been made, it is true, independently; but I absolutely object—and I think in this Dr. Frankland will join me—to its being supposed that these analyses have been made, as has been suggested, in any spirit of antagonism or opposition. Although I admit Dr. Frankland and myself may draw different conclusions from the facts, I think I may say there is very little, if any, difference between us on the facts themselves. There is, I confess, a slight flaw in the exact comparison of our results, viz., that although the samples have been taken from stand-posts supplied by the same companies in the course of the same month, and probably within a day or two of each other, the samples examined by us were not absolutely identical. In comparing the large body of facts before me, and to which for some months past I have devoted a great deal of time, nothing has been to me a source of deeper regret than this fact. I shall be pardoned if I add that at Dr. Letheby's death I was most anxious that Dr. Frankland and myself should examine samples taken at the same time, so that our results might be strictly comparable, and that this could not be arranged was no fault of Dr. Frankland's or of my own, as he himself expressed to me (for which I return him my best thanks) his desire and willingness to make the necessary arrangements, which,

however, were interfered with by the action of the Local Government Board for reasons as absolutely beyond my understanding as many other acts of that august body. Barring this defect, however, a comparison of about 2,500 experiments must be valuable, and if results in any way tally the unfortunate circumstance I have mentioned adds in some respects strength rather than weakness to the position.

The actual results obtained since 1870 by the combustion, ammonia, and oxygen processes are stated in tables side by side, year by year, and in order to render these tables clearer I have arranged them in the form of wave diagrams.

Two of these diagrams are attached to the paper, viz., those for 1877 and 1878. The wave diagrams for 1868—1873, illustrating the results by the combustion process only, are given in Dr. Frankland's paper (*Chem. Soc. J.*, 1876, **1**, 825).

The results obtained by the oxygen process are placed first, then the results obtained by the combustion process, and lastly, the results obtained by the ammonia process.

Confining our comparison first of all to the oxygen and combustion processes, I think you will be struck with the general concordant relationship of the results. Throughout, the line of the Kent Company's water occupies the lowest place indicating the highest organic purity; then follow in order with merely occasional breaks here and there, the very breaks often curiously coinciding, the water of the New River Company and afterwards of the East London Company, and finally the water supplied by the five Thames companies. These throughout occupy the highest place.

But in order that we should possess some more accurate means of testing results than mere general conformity, it became necessary to adopt some system of classification. In venturing to lay before you the classification of waters, founded on the oxygen process, that I have adopted for some time past, I wish to state most emphatically that, in my opinion, all classifications founded on one single factor in the analysis of a water, are to be accepted with great caution, although that factor be the admittedly important one of the organic matter present and its comparative quantity. I do not propose to discuss at present (but I hope to do so before long, if the Fellows of the Chemical Society will allow me), what the circumstances are that must be taken into consideration in reporting on a water, and more particularly what is the special bearing of one result upon another. I do not propose discussing to-night in any way what constitutes a good and what a bad water. I limit myself entirely to the mere chemical question of the value of the several processes employed for estimating the organic matter. But this much I may say here: *First*, that experience shows us that we

should under no circumstances decide the value of a water from an incomplete analysis. That some, from a determination of the ammonia, the albuminoïd ammonia, and the chlorine (however valuable the determination of these may be), can pronounce a water good or bad surprises me much; such details I confess seeming to me to have been chosen with far greater regard to the analyst's time than to the needs of the inquiry. To judge a water justly we must judge it as a whole, and it is impossible to judge it as a whole if the details have not been worked out. Nothing, to my mind, can justify a mere cursory examination of a water when, with all the facts before us, it is often hard enough to judge a righteous judgment. I have said this much because I wish it to be understood that I object to any classification founded on any one constituent of a water. And moreover let me point out that the values of the several constituents of which a water is composed are not their values absolutely but their values relatively. Fifty grains of sodic chloride per gallon in a water may mean nothing. Five grains may mean danger. Hence any suggestion of putting an absolute value on this or that constituent of a water (as has been suggested) is misleading. 200 as the atomic weight of mercury conveys no notion to the mind unless you say that hydrogen is 1.

But *secondly*, all classifications built on an analysis must be influenced by the natural history of the water. On this I will not further enlarge, but I have said this much in order that inferences, which I should be the last to agree to, may not be drawn from the classification founded on the oxygen process that I have adopted, and which I now for the first time venture to put in print. For classifications are always non-natural. Nature never classifies, and classifications, the most perfect, are a mark of imperfection.

I am in the habit of dividing waters into four classes:—

Class I. *Waters of Great Organic Purity.*—In this class I include all waters in which the oxygen required to oxidise oxidisable matters does not exceed 0·05 part per 100,000 parts or 0·035 grain per gallon.

At this point, therefore, I have drawn a line in the diagrams, and coloured the portion a red tint.

Class II. *Waters of Medium Purity.*—In this class I include all waters in which the oxygen required ranges from 0·035 grain to 0·1 grain per gallon, or from 0·05 to 0·15 part per 100,000 parts.

Class III. *Waters of Doubtful Purity.*—In this class I place waters where the oxygen required ranges from 0·1 grain to 0·15 grain per gallon, or from 0·15 to 0·21 part per 100,000 parts.

Class IV. *Impure Waters.*—In this class I include all waters where the oxygen required is above 0·15 grain per gallon.

Again, I would guard myself against its being supposed that I

should draw hard and fast lines. I protest against the notion that all organic matter is to be regarded as equally hurtful, or that the existence of organic matter in a water is a proof of impurity. Surely all kinds of organic matter are not inherently deleterious. As well tell me that putrid food and wholesome meat are alike. Dr. Angus Smith's words on this point express my own views, "The mere existence of organic matter is no proof of impurity. We must know its quality as well as its quantity" (*Chemical News*, June 11, 1869).

The next point to settle was where I was justified in drawing lines on Dr. Frankland's scale which would in any way allow comparison with the divisions on my side of the diagram. The first question was where to draw the line marking off waters of great organic purity. Knowing Dr. Frankland's views on this matter, you will comprehend the difficulty. I have, however, drawn the line at a point where the organic carbon and nitrogen does not exceed 0·1 part per 100,000, and my reasons for doing so are as follows :—

1. That Dr. Frankland has himself in a measure drawn this line :—I do not mean that Dr. Frankland has said in actual words that waters containing less than 0·1 part of organic carbon and nitrogen per 100,000 are waters of great organic purity, but at any rate he says (or the sixth report of the R. P. C. says, and that is the same thing) (page 5), "We consider that potable water which contains organic matter even only partially derived from animal sources should not yield *much more*" (I would note the indefiniteness of the phrase "*not much more*") "than 0·1 part of organic carbon from 100,000 parts of water."

Having drawn this first line at 0·1 per 100,000 for the first class waters corresponding to 0·05 of oxygen, I draw the second line at 0·3 parts per 100,000 to correspond to 0·15 of oxygen. This constitutes on my part the class of waters of medium purity. I do not for a moment wish to imply that Dr. Frankland would adopt such a phrase. But I think there are certain facts and statements scattered throughout "the sixth report" which justify both the lines that I have drawn. Thus, drawing the line at 0·1, I find includes, and only just includes, the Kent water, the supply of which to the Metropolis would have been regarded by the Commissioners as "a priceless boon." Even waters containing more than 0·1 part of organic carbon and nitrogen per 100,000 parts are spoken of as of excellent quality. Thus the water from Lliw Reservoir (0·142 per 100,000) is described (p. 402, line 4) "as of excellent quality, well fitted in every respect for drinking and all domestic purposes." The Rabate fountain (containing 0·133 part of organic carbon and nitrogen per 100,000) at Balmoral Castle was recommended to Her Majesty for drinking purposes, and described as a water "of great purity" (p. 42). The spring above

Frocester, Gloucestershire (containing 0·146 part per 100,000) is spoken of as of "unimpeachable wholesomeness" (page 414).

Again, waters from the greensand are described as of "most excellent quality," containing but mere traces of organic matter, although the analysis shows the presence 0·128 and 0·136 of organic carbon and nitrogen in two wells respectively.

With all these facts before us, I think Dr. Frankland will scarcely complain of the points where I have drawn lines by which to institute comparison between the combustion and the oxygen processes.

And now briefly to state results. 1,686 experiments relate to the oxygen and combustion processes. Of this number, in 1,418 cases the results absolutely agree, that is, so far as the classification I have put before you is concerned, the oxygen and combustion processes tell exactly the same tale in 1,418 out of 1,686 experiments. There remain the 268 cases. Having drawn absolute lines of classification, I have adhered to them strictly, but in a very large number of these 268 cases, the difference depends on the figure in the third decimal place, which let me say would scarcely influence the opinion of those who adopt either the one process or the other. There is but one case in which a water placed by me in the first class is found in Dr. Frankland's third class, and no case where a first class water of Dr. Frankland's is found in my third class. Further, I would note that in nearly all cases the oxygen process tells a worse tale of the water than the combustion process, a result which we should expect from a consideration of the experimental details.

Having now compared the combustion and the oxygen processes, I will turn to the ammonia process. I desire first of all to anticipate a possible criticism in my ammonia determinations, viz., that I have not followed precisely the exact details laid down by Mr. Wanklyn. I think it therefore due to Mr. Wanklyn that I should state in what respects I have departed from his printed instructions, and leave you to judge how far these alterations can affect the results.

1. I do not employ half a litre of water for the determination, but a half of a deci-gallon. I mention this, although Mr. Wanklyn himself remarks that the process can be conducted equally well and with equal accuracy on 100 c.c. as on half a litre. This, therefore, cannot affect the results.

2. In the case of the London waters, with the reactions of which one is so perfectly familiar, I do not collect the albuminoïd ammonia distillates in two, three, or four different lots, but in one lot. I do this because I think it preferable to avoid multiplying errors of observation—that is, I prefer one error of observation to several. This cannot affect the results, except by increasing their accuracy.

3. I am in the habit of employing caramel solutions for the pur-

pose of estimating the amount of ammonia instead of Nesslerising solutions containing known quantities of ammonia on every occasion of making determinations. Amongst the very large collection that has descended to me through Dr. Letheby from the former Professor of Chemistry at the London Hospital, Dr. Pereira, was a solution of burnt sugar. It must have been made between 50 and 60 years, and having been exposed to the light ever since, may fairly be supposed to have undergone every change possible for it to undergo. The tint is absolutely identical with the Nessler tint. Dr. Letheby and myself often tried one another to see whether, when one solution was set by the side of the other, we could tell which was the burnt sugar solution and which was the ammonia and Nessler. I have used these for no other reason than because I believe their use renders ammonia determinations infinitely more delicate and accurate than ordinary Nesslerising, a process far from delicate and accurate, as I have often seen it performed. Thus the Nessler fluid is added to the solution to be examined. A guess is then made as to how much ammonia is present, and that quantity is tried, but found to be too much or too little. Less or more is then tried, and again found to be too much or too little, and then the operator tries a quantity of ammonia between the two, all which time the solution itself has been changing, for every half minute within the first quarter of an hour makes a difference. I have used these solutions solely because I believe them to increase the accuracy of ammonia determinations.

And now with respect to the ammonia results and their relationship to the other results, I must leave the diagrams to tell their own story. I have, it must be understood, expressed the results in accordance with Mr. Wanklyn's plan in parts per million, whereas the results by the oxygen and combustion processes are stated in parts per 100,000:—that is, the extent of scale in the case of the results by the ammonia process is ten times that indicated by the oxygen and combustion processes. I have myself spent days in endeavouring to fix some basis of comparison whereby I might be able to classify the results obtained by the ammonia process, but have failed to do so. I can only say that the results, save in a very general way, correspond neither with the one process nor with the other.

Having dealt with this large body of facts, I turn to my own analyses of 200 miscellaneous samples of water made up to the end of last July, which I would not trouble the Society with, except that all three processes have been adopted on identically the same water.

Comparing first of all the combustion and the oxygen processes, I find that in 94 cases out of the 200, the oxygen process would lead me to place the waters in the first class—that is, the oxygen was less than

0·050 part per 100,000. In 4 cases only out of these 94, was the total organic carbon and nitrogen outside the line drawn at 0·1 part per 100,000. In 2 of these cases it was only just outside the line, and in the other 2 cases the difference was more marked. I append the details of these 4 cases, stating the results in parts per 100,000.

	Oxygen required.	Organic carbon and nitrogen.
No. 1	0·041	0·124
2	0·038	0·126
3	0·043	0·171
4	0·030	0·194

In 73 cases out of the 200, the waters by the oxygen process would have been regarded as second-class waters; that is, the oxygen required to oxidise oxidisable matters ranged between 0·05 and 0·15 parts per 100,000. In 7 only out of these 73 cases did the total organic carbon and nitrogen exceed or fall short of the range between 0·1 part per 100,000 and 0·3 part per 100,000. In 5 of these 7 cases the results by the combustion process were higher, and in 2 they were lower; that is, a higher degree of impurity was indicated in 5 cases by the combustion process, and a higher degree of purity in 2. The details of these 7 cases are stated in the table.

	Oxygen required.	Organic C + N.
No. 1	0·084	0·374
2	0·091	0·368
3	0·090	0·411
4	0·098	0·324
5	0·072	0·320
6	0·088	0·081
7	0·061	0·094

In the remaining 33 cases, in which, so far as the oxygen process indicated, the water was above the second class, and, either in the third or fourth, in no single case did the organic carbon and nitrogen amount to less than 0·3 part per 100,000.

As regards the ammonia process, I find that employing Mr. Wanklyn's scale of (1) *waters of great organic purity*, that is, when the water contains less than 0·05 of albuminoïd ammonia per million as comparable with my first class, and (2) *safe waters*, that is, where the albuminoïd ammonia ranges from 0·05 to 0·1 part per million as comparable with my second class, where the oxygen required ranges from 0·050 to 0·150 part per 100,000; and (3) *dirty waters*, where the albuminoïd ammonia required is above 0·1 part per million as comparable with my third and fourth classes, where the oxygen required is above 0·150, I find that out of my 94 first-class cases only 42 fell in

Mr. Wanklyn's first class, that of my 73 second class only 25 fell in Mr. Wanklyn's second class.

Conclusion.

To sum up, I will now state in a few words my conclusions on this question of the estimation of the organic matter in potable waters and the relative value of the processes employed for the purpose.

1. As regards *the ammonia process*, an absolute or nearly absolute freedom of albuminoïd ammonia is for the most part an indication of organic purity. Nevertheless, many waters which are very impure give a trace only of albuminoïd ammonia, whilst some which are very pure give large quantities of albuminoïd ammonia. Its results, therefore, are marked by singular inconstancy.

2. That the ammonia process allows of no sufficiently large scale whereby the finer grades of purity or impurity can be recognised and classified. The errors arising from many causes, such as, amongst others, the ammonia present in the permanganate solution itself—the difference in time required by different organic bodies for their complete destruction—the chances of the organic nitrogen becoming oxidised—the constant multiplication of errors of observation resulting from collecting several distillates in which the ammonia is to be severally determined, and which errors are again doubled in order to convert results into parts per million—form an array of difficulties likely to lead to serious errors, seeing that the range (viz., from 0·05 to 0·1 part per million) between waters of extraordinary organic purity and dirty waters is comparatively small.

3. That as regards *the combustion process*, the necessity for evaporating the water to dryness constitutes a difficulty, the chances being that some of the organic matter, and possibly that subtle form of organic matter specially active in producing disease—the very organic matter, in fact, the detection of which the sanitarian expects from the chemist, may be either mechanically carried off, or volatilised, or oxidised, or even destroyed under the peculiar conditions of the evaporation.

4. That, barring this objection, the estimation of the organic carbon in the water-residue is trustworthy, repeated experiments with the same water yielding constant results.

5. That the estimation of the organic nitrogen is by no means so constant, the possibility of the nitrate not being completely reduced, especially when present in quantity—of impurities in the sulphurous acid solution—of occluded nitrogen in the metallic copper—and, lastly, the necessary error of experiment constituting a series of difficulties which must somewhat impair the nitrogen determination.

6. That under such circumstances the process can scarcely be considered to yield *absolutely* trustworthy evidence (unless the organic nitrogen be beyond a certain quantity) on which to found an opinion as to the probable source of the organic matter in the water.

7. As regards *the oxygen process*, I claim for it that it is conducted on the original water and without the application of heat. Hence we avoid the evils both of gain and of loss arising from, and incident to, the evaporation of the water to dryness at high temperatures. Moreover the analysis can be conducted with the smallest possible amount of handling, or of pouring the water from vessel to vessel.

8. That the process gives results of great constancy and of *extreme* delicacy. They admit, moreover, of a very wide scale in their classification.

9. That the oxygen process allows us to draw a sharp distinction between the putrescent or readily oxidisable organic matter, which is the more likely, to use Dr. Frankland's term, to be "pernicious," and the non-putrescent or less readily oxidisable matter, which is probably harmless, so far as its action on the human body is concerned.

10. That the general inorganic constituents of a water have no material action on potassic permanganate.

11. The inorganic constituents most likely to be present in a water that would interfere with the estimation of the organic matter by potassic permanganate, are nitrites, metallic protoxides (especially ferrous salts), and sulphuretted hydrogen, all of which are certain to be detected in the course of a proper and complete water analysis, and corrections made accordingly.

12. That in the oxygen process, the only modifying circumstances are those which would render the oxygen required by the water excessive, and that, therefore, although we might be led to report unfavourably on a harmless water, the results obtained would never lead us to report favourably on a bad water.

13. That whilst I do not consider that the oxygen process can be employed with scientific precision as a direct quantitative test of the total organic impurity of a water, nevertheless the results afforded by it indicate with sufficient precision the comparative quantity present likely to be injurious to health.

14. That the results obtained by the oxygen process must at all times be controlled by the natural history, as well as by the general, chemical and physical examination, of the water.

15. That, so far as the three processes, viz., the combustion process, the ammonia process, and the oxygen process are concerned, the oxygen and the combustion processes give closely concordant results, whilst the results yielded by the ammonia process are often at direct variance with both.

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1870.

1870.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·167	0·347	—	0·145	0·446	—	0·190	0·420	0·057	0·161	0·421	—
February.	0·073	0·273	—	0·134	0·203	—	0·207	0·198	—	0·158	0·202	—
March...	0·094	0·233	—	0·132	0·297	—	0·118	0·209	—	0·151	0·224	—
April....	0·071	0·128	—	0·077	0·140	—	0·065	0·134	—	0·071	0·138	—
May	0·047	0·147	—	0·071	0·135	—	0·077	0·157	—	0·077	0·155	—
June	0·048	0·153	—	0·123	0·177	—	0·094	0·185	—	0·113	0·162	—
July	0·071	0·136	—	0·075	0·146	—	0·114	0·155	—	0·114	0·146	—
August ..	0·070	0·163	—	0·130	0·142	—	0·104	0·152	—	0·098	0·158	—
September	0·047	0·142	—	0·098	0·157	—	0·085	0·139	—	0·118	0·133	—
October..	0·064	0·128	—	0·091	0·134	—	0·081	0·162	—	0·070	0·116	—
November	0·055	0·136	—	0·071	0·218	—	0·075	0·157	—	0·071	0·158	—
December	0·093	0·218	—	0·105	0·219	—	0·104	0·177	—	0·127	0·190	—

1870.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·165	0·439	—	0·084	0·235	—	0·151	0·370	—	0·016	0·078	—
February.	0·088	0·207	—	0·030	0·190	—	0·088	0·270	—	0·050	0·083	—
March...	0·118	0·215	—	0·047	0·139	—	0·068	0·174	—	0·018	0·071	—
April....	0·091	0·154	—	0·030	0·060	—	0·061	0·116	—	0·010	0·051	—
May	0·090	0·155	—	0·016	0·080	—	0·028	0·162	—	0·016	0·087	—
June	0·098	0·187	—	0·030	0·106	—	0·048	0·139	—	0·006	0·044	—
July	0·101	0·174	—	0·040	0·135	—	0·067	0·113	—	0·024	0·053	—
August ..	0·090	0·177	—	0·026	0·077	—	0·058	0·127	—	0·000	0·046	—
September	0·091	0·139	—	0·024	0·061	—	0·024	0·151	—	0·010	0·060	—
October..	0·081	0·153	—	0·031	0·055	—	0·020	0·096	—	0·009	0·056	—
November	0·091	0·268	—	0·026	0·052	—	0·020	0·130	—	0·005	0·026	—
December	0·128	0·254	—	0·030	0·032	—	0·058	0·132	—	0·016	0·054	—

November	0·091	0·268	—	0·026	0·052	—	0·020	0·096	—	0·009	0·056	—
December	0·128	0·254	—	0·030	0·032	—	0·020	0·130	—	0·005	0·026	—
							0·058	0·132	—	0·016	0·054	—

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1871.

1871.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	—	0·165	0·042	0·104	0·202	0·114	0·090	0·220	0·071	0·100	0·219	0·142
February.	0·074	0·233	0·057	0·137	0·263	0·071	0·105	0·284	0·071	0·164	0·281	0·085
March ...	0·117	0·159	0·057	0·120	0·192	0·085	0·121	0·188	0·114	0·150	0·161	0·114
April	0·037	0·146	0·042	0·073	0·157	0·114	0·121	0·237	0·085	0·081	0·131	0·114
May.....	0·030	0·246	0·042	0·201	0·270	0·114	0·177	0·309	0·085	0·194	0·281	0·114
June	0·034	0·128	0·071	0·108	0·139	0·057	0·113	0·220	0·042	0·104	0·159	0·071
July.....	0·100	0·170	0·057	0·138	0·166	0·100	0·131	0·205	0·100	0·153	0·215	0·085
August ..	0·063	0·188	0·042	0·173	0·238	0·100	0·137	0·118	0·071	0·155	0·221	0·085
September	0·043	0·152	0·042	0·115	0·145	0·071	0·110	0·157	0·114	0·191	0·148	0·071
October..	0·058	0·331	0·071	0·215	0·596	0·114	0·247	0·514	0·142	0·294	0·591	0·071
November	0·025	0·297	0·085	0·108	0·149	0·114	0·101	0·356	0·142	0·147	0·146	0·114
December	0·040	0·170	0·057	0·070	0·119	0·071	0·071	0·127	0·085	0·068	0·121	0·100

1871.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·081	0·236	0·071	0·064	0·077	0·042	0·113	0·268	0·071	0·013	0·059	0·042
February.	0·195	0·381	0·100	0·053	0·153	0·042	0·100	0·302	0·071	0·006	0·034	0·057
March...	0·155	0·171	0·114	0·055	0·078	0·042	0·114	0·196	0·057	0·006	0·036	0·042
April....	0·095	0·135	0·085	0·037	0·063	0·042	0·095	0·165	0·071	0·041	0·023	0·042
May	0·194	0·277	0·114	0·070	0·135	0·042	0·123	0·267	0·071	0·020	0·034	0·057
June	0·104	0·160	0·057	0·051	0·050	0·000	0·070	0·146	0·014	0·017	0·026	0·042
July	0·113	0·181	0·100	0 033	0·060	0·028	0·053	0·183	0·071	0·014	0·031	0·057
August ..	0·130	0·205	0·100	0·043	0·076	0·042	0·081	0·234	0·057	0·006	0·055	0·057
September	0·113	0·166	0·085	0·030	0·053	0·042	0·073	0·189	0·057	0·014	0·035	0·057
October..	0·260	0·556	—	0 061	0·196	0·042	0·050	0·255	0·100	0·007	0·034	0·042
November	0·107	0·142	0·114	0·037	0·058	0·071	0·076	0·170	0·100	0·020	0·041	0·057
December	0·073	0·119	0·114	0·040	0·047	0·042	0·080	0·138	0·071	0·008	0·029	0·042

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The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1872.

1872.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·048	0·343	0·057	0·130	0·517	0·114	0·164	0·433	0·085	0·134	0·500	0·114
February.	0·070	0·386	0·071	0·191	0·414	0·114	0·165	0·385	0·085	0·193	0·436	0·085
March...	0·078	0·244	0·071	0·113	0·257	0·114	0·113	0·242	0·085	0·121	0·370	0·071
April....	0·107	0·292	0·057	0·215	0·465	0·100	0·221	0·446	0·114	0·167	0·451	0·071
May	0·055	0·176	0·057	0·113	0·170	0·085	0·105	0·188	0·085	0·100	0·185	0·071
June	0·100	0·170	0·057	0·133	0·182	0·085	0·145	0·195	0·114	0·138	0·217	0·114
July	0·113	0·218	0·071	0·143	0·226	0·085	0·155	0·210	0·100	0·148	0·205	0·071
August ..	0·078	0·199	0·071	0·121	0·210	—	0·121	0·215	0·100	0·095	0·198	—
September	0·061	0·172	0·071	0·093	0·147	—	0·138	0·157	0·128	0·087	0·152	—
October..	0·044	0·142	0·042	0·100	0·182	—	0·095	0·167	0·100	0·090	0·164	—
November	0·151	0·384	0·085	0·220	0·432	—	0·167	0·449	0·114	0·204	0·439	—
December	0·145	0·403	0·085	0·238	0·455	—	0·175	0·486	0·142	0·240	0·496	—

1872.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·140	0·570	—	0·030	0·166	0·057	0·097	0·258	0·071	0·018	0·031	0·042
February.	0·200	0·440	—	0·098	0·281	0·085	0·142	0·350	0·085	0·017	0·039	0·042
March...	0·115	0·229	0·114	0·085	0·099	0·057	0·094	0·213	0·057	0·025	0·054	0·057
April....	0·268	0·525	0·142	0·113	0·198	0·057	0·080	0·188	0·042	0·015	0·061	0·042
May	0·144	0·178	0·057	0·050	0·117	0·042	0·074	0·172	0·071	0·018	0·049	0·042
June	0·128	0·196	0·085	0·060	0·108	0·042	0·068	0·170	0·071	0·013	0·059	0·057
July	0·136	0·224	—	0·019	0·092	0·042	0·078	0·175	0·071	0·007	0·059	0·042
August ..	0·100	0·221	—	0·054	0·103	0·057	0·073	0·181	0·071	0·024	0·054	0·042
September	0·060	0·141	—	0·044	0·070	0·057	0·084	0·141	0·071	0·015	0·045	0·042
October..	0·085	0·178	0·085	0·030	0·067	0·057	0·040	0·172	0·071	0·026	0·056	0·057
November	0·217	0·465	0·185	0·134	0·264	0·071	0·125	0·378	0·114	0·016	0·061	0·057
December	0·204	0·524	0·128	0·090	0·325	0·071	0·134	0·460	0·100	0·011	0·069	0·042

November	0·217	0·465	0·185	0·134	0·264	0·071	0·125	0·378	0·114	0·016	0·061	0·057
December	0·204	0·524	0·128	0·090	0·325	0·071	0·134	0·460	0·100	0·011	0·069	0·042

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1873.

1873.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C÷N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·110	0·375	0·057	0·186	0·503	0·114	0·201	0·441	0·142	0·191	0·461	0·100
February.	0·075	0·207	0·071	0·108	0·227	0·085	0·125	0·225	0·114	0·120	0·258	0·100
March...	0·068	0·283	0·071	0·160	0·309	0·114	0·163	0·312	0·114	0·168	0·315	0·085
April....	0·065	0·172	0·071	0·101	0·161	0·100	0·113	0·177	0·114	0·098	0·155	0·085
May	0·044	0·130	0·085	0·095	0·134	0·100	0·071	0·133	0·100	0·073	0·140	0·085
June	0·041	0·149	0·057	0·060	0·157	0·085	0·061	0·158	0·085	0·065	0·170	0·114
July	0·023	0·152	0·057	0·097	0·161	0·071	0·080	0·151	0·071	0·097	0·156	0·071
August ..	0·014	0·169	0·042	0·118	0·197	0·071	0·061	0·155	0·085	0·090	0·169	—
September	0·048	0·129	0·057	0·063	0·140	0·071	0·055	0·145	0·085	0·062	0·142	—
October..	0·025	0·148	0·057	0·087	0·153	0·071	0·075	0·157	0·114	0·060	0·134	—
November	0·054	0·278	0·057	0·140	0·390	0·071	0·165	0·332	0·114	0·173	0·240	0·114
December	0·035	0·222	0·071	0·040	0·238	0·071	0·058	0·205	0·114	0·067	0·220	0·114

1873.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·233	0·514	0·142	0·114	0·289	0·057	0·156	0·375	0·085	0·020	0·065	0·028
February.	0·083	0·257	0·085	0·075	0·188	0·085	0·120	0·391	0·057	0·006	0·053	0·042
March...	0·178	0·339	0·142	0·071	0·205	0·071	0·107	0·172	0·100	0·011	0·040	0·042
April....	0·121	0·166	0·128	0·055	0·110	0·071	0·104	0·203	0·085	0·011	0·049	0·042
May	0·077	0·146	0·100	0·036	0·074	0·057	0·070	0·151	0·085	0·003	0·051	0·042
June	0·063	0·173	0·085	0·027	0·078	0·057	0·054	0·139	0·071	0·006	0·050	0·057
July	0·103	0·171	0·071	0·034	0·092	0·057	0·040	0·134	0·085	0·011	0·063	0·042
August ..	0·084	0·216	0·100	0·037	0·080	0·057	0·037	0·150	0·085	0·007	0·058	0·042
September	0·064	0·172	0·100	0·033	0·069	0·057	0·054	0·135	0·085	0·006	0·060	0·042
October..	0·063	0·187	0·085	0·038	0·077	0·057	0·057	0·185	0·085	0·010	0·073	0·042
November	0·123	0·373	0·114	0·027	0·133	0·042	0·041	0·217	0·071	0·008	0·079	0·042
December	0·053	0·232	0·085	0·031	0·101	0·057	0·101	0·259	0·100	0·021	0·074	0·042

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1874.

1874.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+H	NH_3 (organic)	O	C+H	NH_3 (organic)	O	C+H	NH_3 (organic)	O	C+H	NH_3 (organic)
January..	0·061	0·155	0·057	0·088	0·202	0·114	0·094	0·201	0·114	0·048	0·177	0·071
February.	0·065	0·261	0·085	0·125	0·211	0·114	0·137	0·213	0·114	0·137	0·211	0·128
March ...	0·085	0·333	0·085	0·161	0·385	0·114	0·161	0·392	0·114	0·118	0·366	0·114
April	0·063	0·253	0·071	0·073	0·326	0·100	0·107	0·253	0·114	0·157	0·281	0·071
May	0·070	0·179	0·071	0·073	0·230	0·071	0·075	0·195	0·085	0·073	0·194	0·057
June	0·073	0·215	0·071	0·117	0·217	0·100	0·080	0·188	0·100	0·094	0·207	0·114
July	0·054	0·138	0·071	0·073	0·183	0·100	0·094	0·161	0·100	0·104	0·193	0·114
August ..	0·060	0·162	0·057	0·105	0·155	0·114	0·123	0·200	0·128	0·101	0·163	0·085
September	0·037	0·159	0·071	0·075	0·200	0·085	0·078	0·246	0·085	0·081	0·197	0·100
October..	0·043	0·179	0·071	0·058	0·182	0·085	0·123	0·174	0·114	0·068	0·200	0·114
November	0·041	0·200	0·057	0·070	0·286	0·085	0·087	0·221	0·114	0·100	0·219	—
December	0·070	0·219	0·071	0·178	0·424	0·128	0·148	0·214	0·100	0·193	0·225	0·142

1874.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·053	0·257	0·085	0·007	0·075	0·057	0·094	0·263	0·085	0·003	0·067	0·042
February.	0·126	0·217	—	0·051	0·131	0·071	0·064	0·312	0·071	0·000	0·069	0·042
March ...	0·154	0·361	—	0·021	0·123	0·057	0·077	0·225	0·071	0·004	0·078	0·057
April	0·070	0·285	0·071	0·023	0·092	0·057	0·044	0·142	0·071	0·001	0·075	0·042
May	0·077	0·216	0·085	0·038	0·083	0·042	0·065	0·178	0·071	0·006	0·075	0·028
June	0·085	0·241	0·085	0·027	0·084	0·042	0·065	0·179	0·057	0·004	0·067	0·042
July	0·087	0·189	0·085	0·034	0·118	0·057	0·057	0·139	0·071	0·001	0·039	0·057
August ..	0·108	0·190	0·100	0·026	0·090	0·071	0·148	0·301	0·085	0·005	0·067	0·042
September	0·071	0·237	0·071	0·016	0·188	0·057	0·061	0·155	0·071	0·005	0·081	0·028
October..	0·070	0·206	0·085	0·021	0·107	0·057	0·070	0·247	0·085	0·003	0·076	0·042
November	0·061	0·137	0·071	0·033	0·076	0·057	0·100	0·317	0·085	0·004	0·070	0·057
December	0·131	0·254	0·114	0·023	0·063	0·057	0·074	0·284	0·085	0·001	0·060	0·042

November	0·061	0·137	0·071	0·033	0·076	0·057	0·100	0·317	0·085	0·004	0·070	0·057
December	0·131	0·254	0·114	0·023	0·063	0·057	0·074	0·284	0·085	0·001	0·060	0·042

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1875.

1875.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·088	0·185	0·071	0·120	0·346	0·114	0·123	0·270	0·085	0·130	0·278	0·114
February.	0·084	0·328	0·057	0·125	0·321	0·085	0·170	0·277	0·114	0·161	0·334	0·100
March...	0·080	0·335	0·071	0·118	0·351	0·100	0·135	0·368	0·085	0·121	0·290	0·100
April....	0·038	0·154	0·057	0·088	0·141	0·071	0·078	0·159	0·085	0·061	0·158	0·071
May	0·051	0·159	0·057	0·058	0·186	0·085	0·077	0·206	0·100	0·084	0·181	0·085
June	0·061	0·150	0·057	0·080	0·139	0·071	0·074	0·190	0·071	0·073	0·156	0·071
July	0·048	0·128	0·057	0·061	0·136	0·085	0·073	0·141	0·071	0·080	0·160	0·085
August ..	0·058	0·382	0·057	0·233	0·304	0·114	0·178	0·345	—	0·205	0·299	0·100
September	0·045	0·146	0·057	0·104	0·189	0·085	0·082	0·152	—	0·091	0·162	0·071
October..	0·065	0·183	0·071	0·080	0·232	0·085	0·091	0·186	0·114	0·134	0·153	0·142
November	0·081	0·485	0·085	0·180	0·536	0·142	0·241	0·499	0·128	0·247	0·509	0·142
December	0·044	0·203	0·071	0·074	0·191	0·114	0·111	0·215	0·142	0·086	0·180	0·114

1875.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·187	0·343	0·142	0·026	0·123	0·057	0·094	0·263	0·085	0·005	0·046	0·057
February.	0·168	0·289	0·114	0·070	0·212	0·071	0·964	0·312	0·071	0·011	0·057	0·042
March...	0·087	0·293	0·071	0·023	0·138	0·042	0·077	0·225	0·071	0·013	0·044	0·042
April....	0·058	0·152	0·071	0·019	0·088	0·042	0·044	0·142	0·071	0·004	0·039	0·028
May	0·081	0·186	0·071	0·021	0·102	0·042	0·065	0·178	0·071	0·010	0·075	0·042
June	0·078	0·177	0·071	0·020	0·079	0·042	0·065	0·179	0·057	0·010	0·062	0·042
July	0·081	0·167	0·085	0·033	0·083	0·057	0·057	0·139	0·071	0·005	0·059	0·042
August ..	0·211	0·359	0·100	0·080	0·148	0·057	0·048	0·301	0·085	0·005	0·062	0·042
September	0·103	0·166	0·100	0·040	0·065	0·042	0·061	0·155	0·071	0·004	0·053	0·028
October..	0·085	0·311	0·128	0·043	0·115	0·057	0·070	0·247	0·085	0·016	0·075	0·042
November	0·207	0·433	0·114	0·077	0·250	0·071	0·100	0·317	0·085	0·027	0·069	0·057
December	0·115	0·260	0·128	0·070	0·213	0·071	0·074	0·284	0·085	0·008	0·078	0·042

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1876.

1876.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·075	0·258	0·071	0·080	0·287	0·085	0·081	0·363	0·100	0·073	0·229	0·071
February.	0·070	0·190	0·085	0·090	0·171	0·100	0·100	0·220	0·100	0·084	0·190	0·085
March...	0·138	0·293	0·085	0·163	0·371	0·114	0·134	0·338	0·100	0·143	0·321	0·071
April....	0·075	0·218	0·100	0·121	0·293	0·085	0·153	0·245	0·100	0·101	0·236	0·085
May	0·067	0·181	0·100	0·118	0·171	0·100	0·077	0·180	0·114	0·103	0·159	0·100
June	0·073	0·075	0·100	0·078	0·132	0·100	0·073	0·120	0·085	0·057	0·129	0·100
July	0·051	0·106	0·100	0·103	0·145	0·100	0·068	0·178	0·100	0·086	0·137	0·071
August ..	0·071	0·114	0·114	0·061	0·122	0·114	0·055	0·158	0·085	0·065	0·114	0·100
September	0·045	0·105	0·085	0·050	0·107	0·100	0·065	0·191	0·085	0·045	0·117	0·085
October..	0·117	0·196	0·114	0·140	0·301	0·100	0·071	0·321	0·114	0·120	0·236	0·114
November	0·068	0·135	0·085	0·055	0·153	0·085	0·083	0·126	0·114	0·068	0·122	0·100
December	0·143	0·405	0·128	0·188	0·423	0·000	0·163	0·570	0·114	0·183	0·454	0·128

1876.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·081	0·289	0·085	0·050	0·176	0·057	0·080	0·218	0·085	0·015	0·064	0·042
February.	0·080	0·181	0·085	0·058	0·122	0·057	0·074	0·174	0·085	0·014	0·043	0·042
March...	0·118	0·283	0·100	0·086	0·235	0·071	0·074	0·242	0·085	0·015	0·076	0·028
April....	0·101	0·311	0·085	0·024	0·122	0·071	0·075	0·148	0·057	0·004	0·070	0·028
May	0·087	0·193	0·085	0·041	0·116	0·042	0·064	0·200	0·071	0·014	0·069	0·028
June	0·091	0·152	0·085	0·057	0·044	0·042	0·034	0·078	0·071	0·011	0·023	0·028
July	0·084	0·162	0·100	0·030	0·079	0·057	0·051	0·119	0·071	0·010	0·060	0·042
August ..	0·063	0·101	0·100	0·040	0·053	0·057	0·055	0·103	0·057	0·010	0·061	0·028
September	0·060	0·173	0·114	0·049	0·076	0·085	0·040	0·111	0·071	0·004	0·056	0·000
October..	0·130	0·294	0·100	0·038	0·066	0·057	0·053	0·151	0·071	0·014	0·071	0·000
November	0·054	0·200	0·071	0·020	0·065	0·057	0·048	0·134	0·057	0·020	0·064	0·028
December	0·155	0·371	0·100	0·131	0·185	0·057	0·074	0·239	0·085	0·010	0·060	0·028

November	0·054	0·200	0·071	0·020	0·065	0·057	0·048	0·134	0·057	0·020	0·064	0·028
December	0·155	0·371	0·100	0·131	0·185	0·057	0·074	0·239	0·085	0·010	0·060	0·028

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1877.

1877.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·190	0·356	0·114	0·171	0·413	0·128	0·197	0·470	0·085	0·193	0·406	0·100
February.	0·110	0·217	0·100	0·094	0·214	0·085	0·110	0·232	0·100	0·104	0·253	0·085
March...	0·104	0·249	0·085	0·077	0·264	0·114	0·101	0·246	0·100	0·075	0·240	0·114
April....	0·081	0·310	0·128	0·161	0·357	0·114	0·095	0·462	0·128	0·091	0·337	0·128
May	0·084	0·172	0·100	0·074	0·131	0·100	0·074	0·181	0·114	0·070	0·132	0·100
June	0·077	0·151	0·100	0·108	0·204	0·128	0·091	0·244	0·128	0·071	0·146	0·114
July	0·075	0·069	0·100	0·081	0·110	0·100	0·071	0·086	0·114	0·074	0·130	0·100
August ..	0·068	0·128	0·100	0·030	0·143	0·128	0·074	0·140	0·100	0·034	0·139	0·100
September	0·068	0·165	0·128	0·131	0·233	0·128	0·155	0·281	0·142	0·143	0·161	0·128
October..	0·061	0·095	0·114	0·077	0·137	0·128	0·083	0·114	0·142	0·061	0·085	0·071
November	0·060	0·122	0·114	0·060	0·207	0·114	0·075	0·190	0·114	0·065	0·151	0·100
December	0·118	0·351	0·114	0·097	0·310	0·142	0·181	0·312	0·128	0·191	0·336	0·114

1877.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·134	0·354	0·128	0·134	0·296	0·071	0·141	0·300	0·114	0·004	0·077	0 042
February.	0·080	0·225	0·114	0·070	0·185	0·071	0·090	0·214	0·100	0·001	0·048	0·042
March...	0·100	0·227	0·128	0·095	0·227	0·085	0·100	0·246	0·085	0·010	0·062	0·028
April....	0·100	0·280	0·114	0·060	0·185	0·085	0·085	0·210	0·114	0·009	0·061	0·042
May	0·075	0·166	0·114	0·051	0·119	0·085	0·040	0·109	0·100	0·004	0·070	0·028
June	0·105	0·180	0·114	0·046	0·074	0·085	0·067	0·173	0·100	0·004	0·080	0·028
July	0·074	0·134	0·128	0·027	0·078	0·085	0·065	0·043	0·100	0·021	0·047	0·042
August ..	0·110	0·127	0·114	0·034	0·081	0·128	0·090	0·118	0·085	0·004	0·060	0·028
September	0·113	0·257	0·128	0·024	0·059	0·085	0·058	0·114	0·100	0·014	0·046	0·028
October..	0·067	0·106	0·128	0·025	0·041	0·100	0·057	0·072	0·100	0·014	0·038	0·057
November	0·075	0·173	0·128	0·071	0·048	0·085	0·045	0·070	0·100	0·004	0·048	0·028
December	0·118	0·331	0·128	0·051	0·178	0·100	0·051	0·207	0·100	0·004	0·077	0·042

The Organic Purity of Monthly Samples of the Water supplied by the Metropolitan Water Companies, as shown by the Oxygen, the Combustion, and the Ammonia Processes, 1878.

1878.	West Middlesex Company.			Chelsea Water Company.			Southwark Company.			Grand Junction Company.		
	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.	Oxygen P.	Combustion P.	Ammonia P.
	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.	Parts per 100,000.		Parts per million.
	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)	O	C+N	NH_3 (organic)
January..	0·203	0·351	0·114	0·075	0·306	0·128	0·085	0·304	0·128	0·163	0·372	0·128
February.	0·090	0·191	0·128	0·074	0·221	0·128	0·070	0·187	0·128	0·074	0·231	0·143
March...	0·088	0·206	0·114	0·068	0·222	0·143	0·087	0·263	0·157	0·073	0·232	0·100
April....	0·075	0·176	0·128	0·065	0·224	0·114	0·065	0·222	0·114	0·127	0·182	0·128
May	0·120	0·278	0·143	0·080	0·237	0·100	0·110	0·283	0·128	0·094	0·266	0·128
June	0·104	0·337	0·114	0·128	0·255	0·128	0·140	0·283	0·143	0·144	0·328	0·128
July	0·095	0·252	0·143	0·081	0·226	0·128	0·095	0·198	0·157	0·097	0·295	0·143
August ..	0·071	0·174	0·114	0·050	0·174	0·128	0·075	0·157	0·114	0·065	0·198	0·114
September	0·127	0·307	0·143	0·060	0·194	0·128	0·147	0·257	0·157	0·127	0·246	0·157
October..	0·068	0·195	0·171	0·074	0·232	0·114	0·052	0·193	0·214	0·060	0·195	0·214
November	0·081	0·260	0·143	0·010	0·251	0·128	0·104	0·336	0·100	0·087	0·247	0·157
December	0·127	0·339	0·143	0·104	0·287	0·143	0·164	0·362	0·085	0·107	0·461	0·143

1878.	Lambeth Company.			New River Company.			East London Company.			Kent Company.		
January..	0·104	0·266	0·100	0·083	0·203	0·112	0·067	0·232	0·085	0·013	0·093	0·058
February.	0·064	0·194	0·128	0·054	0·129	0·128	0·094	0·182	0·128	0·004	0·064	0·043
March...	0·088	0·251	0·157	0·034	0·126	0·100	0·045	0·192	0·100	0·000	0·064	0·028
April....	0·060	0·180	0·114	0·060	0·100	0·048	0·060	0·158	0·114	0·020	0·078	0·114
May	0·090	0·234	0·114	0·034	0·172	0·071	0·070	0·231	0·100	0·002	0·050	0·014
June	0·140	0·334	0·157	0·064	0·251	0·085	0·080	0·276	0·085	0·004	0·087	0·028
July	0·097	0·350	0·128	0·065	0·156	0·114	0·065	0·275	0·114	0·014	0·092	0·028
August ..	0·071	0·200	0·114	0·025	0·123	0·085	0·055	0·170	0·100	0·004	0·063	0·028
September	0·137	0·328	0·143	0·081	0·119	0·100	0·075	0·175	0·100	0·002	0·093	0·014
October..	0·033	0·181	0·285	0·024	0·116	0·100	0·054	0·159	0·071	0·004	0·107	0·043
November	0·098	0·298	0·143	0·024	0·121	0·071	0·048	0·209	0·100	0·004	0·062	0·014
December	0·147	0·318	0·143	0·081	0·212	0·071	0·093	0·257	0·128	0·003	0·095	0·028

XIII.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies.* Part IX. *Preparation of Zinc-Methyl.*

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

In a previous communication (*Chem. Soc. J.*, 1873, page 682) we stated that methyl iodide is but slightly acted upon by the copper-zinc couple, at its boiling point; indeed, so slightly that we did not look upon this as a practical method of preparing the zinc-compound. But from theoretical considerations relative to the formation of the C_nH_{2n+2} hydrocarbons, we arrived at the opinion that this iodide would be slowly acted upon by the zinc of the couple, even at the ordinary temperature.

An examination of this forecast was made by taking a number of dry couples prepared from half a meter of foil as described in this Journal 1877, i, 567, pouring on them 5 c.c. (11 grams) of methyl iodide, well corking the flasks containing the materials, and making daily observations of any changes. In a day or two some white grains were noticeable intermingled with the couple, and adhering to the sides of the vessels, after which no further change could be detected for some time, when it was observed that the liquid was somewhat yellow, and had diminished in quantity. This apparent absorption of liquid continued, and almost as soon as it appeared complete, crystalline plates were seen studding the surface of the uppermost points of the couples, which went on increasing until the whole appeared one uniform beautifully crystalline mass. The times varied for the first and second parts of this reaction, and the whole particulars are set out in the following table:—

Experiment.	Mean temperature.	First signs of crystallisation.	Completion of action.
I.	18° C.	34 days	36 days
II.	„	29 „	31 „
III.	„	43 „	45 „
IV.	„	32 „	36 „
V.	20° C.	37 „	39 „
VI.	„	39 „	43 „
VII.	22° C.	28 „	30 „
VIII.	„	29 „	30 „

Zinc Methiodide.

On removing the corks of the flasks, a slight outrush of gas took place, followed immediately by white fumes within the vessels. The gas which escaped burnt when ignited, with a bluish flame, and it doubtless consisted of zinc-methyl, saturating the nitrogen of the air originally present. From the mode of formation of the crystalline body, and the absence of liquid or gaseous products, it can scarcely be other than the methyl analogue of Frankland's zinc ethiodide; and, from analogy, it might be expected to split up by heat into zinc iodide and zinc-methyl, zinc iodide, zinc, and di-methyl, or into a mixture of these several substances.

A cork with two tubes was fitted into one of the flasks containing the crystalline product from 5 c.c. of the iodide; one of the tubes was connected with a dry hydrogen supply; the other with a condenser with a fitted and weighed receiver. The gas, on passing through the apparatus for a few minutes, was found to be burning with a bluish flame, indicating the presence of zinc. The current of hydrogen was now stopped, and the flask slowly heated from the melting point of the paraffin bath to 100° C. At about 60° a perfectly clear and colourless liquid began to distil; in 15 minutes it ceased. The distillate weighed 2·7 grams. It was very mobile, had a powerful odour, was free from iodine, and very spontaneously inflammable; in fact, had all the properties ascribed by Frankland to zinc-methyl. The residue in the flask was nearly white, and consisted of zinc iodide. The 2·7 grams corresponds with 72 per cent. of the theoretical quantity, which, when we remember that it is less by that which necessarily adhered to the tubule of the condenser, &c., represents pretty closely the possible yield.

Progress of the Action.

Information as to the rate at which this chemical change takes place appeared very desirable. It was obtained by pouring 5 c.c. of the methyl iodide (at the summer temperature) on to each of five couples made as much alike as we could make them, and estimating the action by distilling the zinc-methyl from the product at the end of the first week in one, at the end of the second week in another, and so on. The results are tabulated below:—

Time.	$(CH_3)_2Zn$.
7 days	1·387 grams.
14 „	2·063 „
21 „	2·344 „
28 „	2·73 „
31 „	3·72 „

Signs of crystallisation were noticeable only in the last of these couples, and that on the twenty-ninth day. It appears therefore that, although the action probably starts with comparative energy, the methiodide crystallises and perhaps forms only when the whole of the methylic iodide has disappeared. The methiodide is, in fact, very soluble in methylic iodide.

Effect of Temperature and Time.

As already stated, the couple, when boiled with methyl iodide, decomposes it but slowly; but to obtain definite knowledge on this point, we boiled 5 c.c. of the iodide with the usual quantity of couple for 6 hours, and in another experiment for 22 hours. In the 6 hours the equivalent of 0·945 gram of zinc methyl formed, and in the 22 hours 1·4 grams.

The augmented temperature, as was to be expected, expedites the action, but it may be observed that at this higher temperature, as well as at the lower one, the formation of zinc-methiodide takes place in a rapidly-diminishing ratio with regard to time, even when all allowance is made for the diminishing amounts of liquid and zinc. Experiments were made on this point.

Effect of Quantity of Couple.

5 c.c. of the iodide were added at the ordinary temperature to twice the usual quantity of couple, when the action was found to be complete in three days; and when three times the quantity of couple was used and the same quantity of iodide, the action was over in one day; from which it would appear that the time required to bring about the decomposition of a given quantity of this iodide becomes 12 times less by doubling the amount of couple, and 36 times less by trebling it. We can only therefore attribute the rapidly-decreasing action as time advances to the interference of the zinc methiodide.

To study still more completely the changes involved, and in fact to analyse the crystalline body, the following experiment was made:—A flask containing the methiodide from 11·2 grams of methyl iodide, and the apparatus to which it was connected, were freed from air by dry carbonic anhydride, and the methiodide was decomposed in a current of this gas by heating up to 100°C. The zinc-methyl, as it was set free, was passed into dilute sulphuric acid, and the zinc therein was estimated as oxide. It weighed 2·934 grams, equivalent to 3·44 grams of zinc-methyl. The gas resulting from the decomposition of the volatile zinc-compound was collected over a solution of caustic potash. It measured 1,677 c.c. (corrected), and burnt with a somewhat luminous flame, at the same time depositing a small quantity of a yellowish-red substance. After

standing, however, over water for a day, it burnt with an almost colourless flame without the separation of any solid body, and from the quantity collected, and from what is known of the decomposition-products of zinc-methyl by water, there can be no doubt that it was pure, or nearly pure, marsh-gas. Now the 11·2 grams of methyl iodide could yield theoretically 3·75 grams of zinc-methyl, which, in presence of water, would give 1,764 c.c. of marsh-gas and 3·198 grams of zinc oxide, numbers which but very slightly exceed our experimental ones.

It appears then from this inquiry, that the action of our couple on iodide of methyl at the ordinary temperature is to build up zinc methiodide only;* whether in one stage, thus:—

$$CH_3I + Zn, Cu = CH_3IZn + Cu,$$

or in two:—

$$(a.)\ 2CH_3I + 2Zn, Cu = \left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\} Zn + ZnI_2 + Cu$$

$$(b.)\ (CH_3)_2Zn + ZnI_2 = 2ZnICH_3,$$

is open to conjecture; and that this methiodide splits up very readily by heat, without fusing, into zinc iodide and zinc methyl, thus:—

$$2ZnICH_3 = ZnI_2 + Zn(CH_3)_2.$$

The methiodide is also decomposed by light, the white lustrous crystals becoming dark grey or black, probably from the separation of metallic zinc.

On starting this work, we placed 5 c.c. of methyl iodide in contact with the same quantity of zinc foil as has been employed for the couples used in these experiments. The surface of the metal became tarnished, but no signs of the methiodide appeared; and on opening the flask more than seven months afterwards, only a doubtful trace of any zinc-compound was found.

This investigation specially illustrates the value of our couple in bringing about, at a low temperature, a chemical change which can be brought about by its more positive element, only at such a temperature and under such conditions, as occasion the formation of secondary products. It has also furnished a perfect and really simple method of preparing Frankland's most valuable reagent, zinc-methyl: for in the last experiment described the yield of this substance amounts to 91·7 per cent. of the possible quantity, and in another, the results of which are given on the last line of page 108, to 99·2 per cent.

* In two instances out of about 30, the thin closed flasks containing the couple and iodide burst before the action was complete, which we are disposed to attribute to the accidental presence of moisture, giving rise to marsh-gas. All chance of bursting may be prevented by employing a Bunsen valve.

XIV.—*On Erbium and Yttrium.*

By J. S. Humpidge, B.Sc. (Lond.), Ph.D., and W. Burney.

(Preliminary Remarks.)

In 1794, after examining the mineral known as gadolinite, Gadolin announced the discovery of a new earth therein. This new earth has been shown by subsequent researches to be a mixture of at least six different substances. Ekeberg, in 1802, separated glucina, and Berzelius discovered ceria in 1815, and yttria some years later. Berlin worked with the crude yttria in 1835, which he prepared according to Berzelius' method. But although he prepared many salts, he mentions no suspicion of there being more than one earth included under this group. (*K. Vet. Akad. Hand.*, 1835, 209; and *Pogg. Ann.*, **43**, 105.)

A few years later Mosander stated that the cerium metals were three—cerium, lanthanum, and didymium; and in 1843, that the yttrium metals were also three—yttrium, erbium, and terbium. The pale rose-colour which the salts of the mixed oxides present after the separation of the cerium metals had been previously noticed,* and had been generally ascribed to manganese, the tint of whose salts it almost exactly resembles. Berzelius (*Lehrbuch*—German Edition, 1832, p. 214) mentions the occurrence of manganese, and Berlin found it in one analysis, but only in traces; otherwise the former general acceptance of the presence of this substance may be ascribed to the colour of the erbium salts.

In Mosander's original paper, which was read at a meeting of Scandinavian philosophers (*Ann. Chem. Pharm.*, **48**, 210), his description of the methods he employed for the preparation of the three earths in a state of purity is exceedingly imperfect. He says a partial separation may be effected by fractional precipitation with ammonium or potassium oxalate; yttria being the strongest base remains longest in solution, and by repeating the method many times, this earth may be obtained in a state of purity. He gives us no means of judging how this was known to be pure, or of any special method for separating the other two; he mentions nothing distinctly. Nevertheless, he gives the following as the properties of the three oxides:—

Yttria is colourless and the strongest base, its salts are colourless; terbia is colourless, and the next in basicity, its salts are reddish;

* Heinrich Rose [*Pogg. Ann.*, **59**, 101] mentioned this pink colour, and thought it might be due to some new substance, but gave up his work on hearing that Mosander and Berzelius were extending their researches.

erbia is deep-yellow in colour, becoming colourless when glowed in hydrogen without appreciable loss in weight,* its salts are colourless. Terbia is distinguished by a sulphate efflorescing at 50°.

Some years afterwards Berlin (*Fordhandlinger ved de Skan. Naturfor. attende Möde i Kjöbenhavn*, 1860, p. 418) subjected these earths to a new examination. Following the method of separation proposed by Mosander, he was able to obtain only two earths, yttria and erbia; his terbia was always capable of being resolved into the other two, when the separation was continued long enough. He was also unable to obtain the sulphate efflorescing at 50°, which Mosander mentioned as being characteristic of terbia.

In 1864, Popp (*Ann. Chem. Pharm.*, **131**, 179), under the direction of Woehler, published some further researches, but as he considered that the crude yttria contained only one earth, we need not delay discussing his results.

The year following, Delafontaine (*Ann. Chem. Pharm.*, **134**, 99), after carefully repeating Mosander's method of separating the crude yttria, confirmed the results of this chemist. But as he adopted Berzelius' method of separating the cerium metals, and did not allow the solution of the sulphates to remain in contact with the potassium sulphate longer than twenty-four hours, it is clear that his crude yttria must have contained considerable quantities of these three earths; and as he distinctly says that his potassium-erbium sulphate is insoluble in a saturated solution of potassium sulphate, we may fairly conclude that his erbia consisted mostly of the oxides of the cerium metals. This supposition is strengthened by the fact that the atomic weight which he gives for this erbium (95·36) coincides almost exactly with the mean of those of the cerium metals (94·00). Several properties of this substance agree also remarkably with those of the cerium metals, among which may be mentioned the fact that its salts give an absorption-spectrum resembling that of the didymium salts, except that the lines are not so intense. In a later paper (*N. Arch. Ph. Nat.*, **25**, 112, 1866) he corrects his statement, but mentions that his erbium-salts have all a pink colour. From analyses of the sulphates he gives the following atomic weights:—

$$Y = 111{\cdot}6;\ Er = 143{\cdot}04;\ Tr = 137{\cdot}04\ [\text{oxides} = M_2O_3],$$

though he does not himself consider these results very accurate. Yttria is white, erbia yellow, and terbia pink.

In the following year Bunsen worked at the subject in conjunction with a Swedish chemist, Bahr. They found that the best method of separating the crude yttria was by means of the basic nitrates. This method consists in dissolving the mixed basic nitrates in the smallest possible quantity of hot water, when the crystallisation, which

* A fact first noticed by Scheerer.

separates out on cooling, is always richer in erbium than the material employed. In this way, by working a number of series of crystallisations, they obtained two earths in a state of purity, to which they give the names erbia and yttria. All search for the third earth (Delafontaine's erbia) was fruitless. They published for the first time a drawing of the absorption-spectrum of the erbium salts, and by a comparison with that of the didymium salts, showed that no two lines coincided with one another. They made the interesting discovery, which Bahr had before casually observed, that when erbia is heated to whiteness, it emits a green light and gives a bright spectrum exactly the inverse of the absorption-spectrum of its salts. They found, too, the same to be the case with didymium oxide. The following atomic weights are given:—

$$Y = 92{\cdot}55;\ Er = 168{\cdot}9;\ [\text{oxides} = M_2O_3].$$

Cleve and Hoeglund (*Bull. Soc. Chim.*, 1872, **18**, 193) have published some interesting work on these substances. They attempted the extraction of the metals by electrolysis, but obtained nothing but black powders. We are indebted to them for descriptions of a large number of salts prepared from erbia and yttria carefully separated by Bunsen's method. They searched in vain for the third earth. As atomic weights they give the following numbers:—

$$Y = 89{\cdot}55;\ Er = 170{\cdot}55.$$

The difficulty of obtaining the earths in such a state of purity is instanced by the fact that, although they employed five kilograms of gadolinite, they obtained only a few grams of the pure oxides. From the constitution of the salts which they prepared, it would appear that the metals are triatomic, *i.e.*, the oxides are sesquioxides.

In the beginning of this year Marignac published some investigations on these earths (*Arch. Scien. Ph. und Nat.*, **61**, March, 1878). He extracted them as usual from gadolinite, and employed Bunsen's mode of separation, *i.e.*, by means of the basic nitrates. Following this out carefully, he obtained, as the two end-products of a long series of crystallisations, a rose-coloured and a white oxide, Bunsen's erbia and yttria. But besides these two he noticed that the middle products were much deeper in colour than the original mixed oxides, even when a trace of the cerium metals had been removed. These deep-coloured middle products he divided into two classes, (1) those containing erbium in considerable quantity; and (2) those containing only traces of this substance. He found no method of separating the erbium from the first class, but was able to separate the yttrium from the second, by successive fractional precipitations with oxalic acid, the yttrium remaining longer in solution. By this means an earth was obtained

becoming deeper and deeper in colour. Solutions of this earth are colourless, and give no absorption-spectrum. This should be the missing erbia of Mosander, Bunsen's terbia. Careful determinations of its atomic weight gave

$$Tr = 148{\cdot}5\,;\ [\text{oxide} = Tr_2O_3].$$

In the same Journal, of the same date, M. Delafontaine has published some further work on the earths contained in samarskite. After removing the cerium metals, he first effected a partial separation with oxalic acid, then dissolved the deep-coloured oxides so obtained in formic acid, which on heating gave a precipitate whose oxide was still deeper in colour. By continuing this separation he at last obtained an oxide, the metal of which gave the atomic weight 147, a number agreeing very well with that found by Marignac for terbium.

We have instituted some further experiments with these earths, with the special object of isolating the metals and determining their specific heats; hoping, too, to find a better method of separation than is at present known.

We made use of gadolinite for the extraction of the earths. For this rare material we are indebted to Professor Bunsen, and to Professor Waage, of Christiania, to whom we wish to tender our sincere thanks.

The crude earths were extracted in the usual way, and the separation of the cerium metals carefully performed by dissolving the anhydrous sulphates in fifteen parts of ice-cold water, and then suspending in this solution masses of potassium sulphate, so arranged that portions of the salt projected out of the liquid. This was allowed to stand for about a fortnight, the liquid being frequently agitated. At the end of this time the liquid, which did not show the spectrum of the didymium salts in the faintest degree, was filtered, and ammonia added in excess. The precipitate so obtained was then dissolved in hydrochloric acid and reprecipitated with oxalic acid. This precipitate on glowing gave the pure earths. There were still very slight traces of the cerium metals present, which were afterwards specially removed. The oxides were specially tested for manganese, but not a trace was found.

The crude yttria so prepared was a light, pale lemon-coloured powder, easily soluble in all acids.

With regard to the separation of these mixed earths, we regret that we have as yet been unable to find a better method than the approximate one with the basic nitrates, as employed by Bunsen. The process is an exceedingly tedious one, and the pure oxides are obtained only in very small quantities, even when considerable masses of material are employed.

As the special object of these investigations was to determine the

true atomic weights of these elements, a long series of experiments was made to procure the metals in coherent masses, and determine their specific heats. Here, again, only negative results were obtained. All attempts to decompose the fused chlorides by electrolysis have yielded the metals only as black powders, or as small metallic scales. The same method was followed as that employed by Bunsen for preparing calcium, strontium, &c. The chlorides were prepared, just like anhydrous magnesium chloride, by evaporating their solution with a large excess of sal-ammoniac, and then driving off this latter by heat. The black mass at the end of the electrolysis, on being powdered under, and washed with naphtha, always left a heavy black powder, with many bright metallic scales, nearly resembling aluminium. This was slowly oxidised by water at the ordinary temperature; more rapidly on warming, with a brisk evolution of hydrogen. The action was, of course, accelerated by dilute acids. The metal burnt in the flame of a gas-lamp with a brilliant white light, like magnesium. We also obtained in nearly every operation some small bright-red, transparent crystals, decomposed slowly by water and acids, but otherwise tolerably stable. This may have been an oxychloride corresponding with that of didymium; we did not obtain sufficient quantities of it to make a thorough examination.

As the specific heat of the metals could not be obtained, and as no volatile compound of these elements is known, the next best method of finding the atomic weights is by isomorphism.

As far as we know, the only salts which have been carefully investigated are the sulphates.

Rammelsberg (*Pogg. Ann.*, **115**, 579) has shown that the sulphates of didymium and of the mixed yttrium metals have a chemical composition similar to that of cadmium sulphate, and that the angles of the three salts agree tolerably well. From this he drew the natural conclusion that the oxides of yttrium and didymium were monoxides, which, as far as the latter is concerned, the later researches of Hildebrand and Norton (*Pogg. Ann.*, **158**, 71) have not confirmed. We cannot tell whether this, too, may be the case with the yttrium metals, which seems probable, or whether the atomic weight derived from the isomorphism with the cadmium salt is to be accepted. A glance at the numerous compounds prepared by MM. Cleve and Hoeglund shows that they are formulated in the simplest manner on the supposition that the oxides are sesquioxides, and it need scarcely be remarked that the analogy of the yttrium salts to those of didymium is far greater than to those of cadmium. We have further experiments in progress to decide this question of isomorphism.

By conducting a long series of crystallisations we were able to obtain some erbia, giving a combining weight of 195·84 (mean of four

determinations); this on being subjected to crystallisation in the usual manner gave a product the combining weight of whose oxide was 195·61 (mean of 195·54 and 195·69).* These numbers agree so well together as to make it more than probable that this was pure erbia. Comparing the atomic weight of erbium so obtained with previous determinations of other chemists, we have:—

Delafontaine	= 137·04	
Bunsen and Bahr.....	= 168·90	
Cleve and Hoeglund	= 170·55	mean = 171·08.
Humpidge and Burney	= 171·61	

As Delafontaine employed Mosander's method of separation, which yields only very approximate results, we may disregard his number; and as Bunsen worked with only comparatively small quantities, his erbia may not have been perfectly pure. It is therefore extremely probable that the atomic weight of erbium lies between our determinations and those of Cleve.

We have not as yet obtained any yttria sufficiently pure to be able to make an accurate determination of its combining weight.

At the end of this paper are two analyses of the gadolinite we have employed. One specimen was from Ytterby, and the other from Hitterö. The question of the presence of manganese has been already touched upon, and with regard to glucinum, we may remark that the older methods of extracting the crude yttria did not completely separate this substance. Heinrich Rose (*Pogg. Ann.*, **59**, 101) was the first to remark that this was the case, and to show that the chlorides are not volatile. Woehler's yttrium (*Pogg. Ann.*, **13**, 580) must therefore have been glucinum, as it was prepared from a volatile chloride. He says, too, that the metal so prepared does not decompose water at the ordinary temperature, whereas that prepared by electrolysis of the pure chlorides always does so. The presence of phosphoric acid in gadolinite is, as far as we know, mentioned for the first time. It was probably all or nearly all present as phosphates of the yttrium and cerium metals, as it nearly all remained behind on decomposing the mineral with *aqua regia*. These earths remaining behind with the silica consisted of nearly pure yttria with traces of the cerium metals.

Thinking perhaps that we might be able to find some xenotime enclosed in the gadolinite, we prepared several microscopic sections of the mineral, but nothing was to be seen except a dark-green homogeneous field, without action on polarised light:—

* (i.) Oxides = 1·2147 gram. Sulphates = 1·9596 gram.
(ii.) Oxides = 1·1781 „ Sulphates = 1·9011 „

	(1.) Gadolinite from Ytterby.	(2.) From Hitteröe.
SiO_2	25·161	24·242
P_2O_5	1·281	—
Yt_2O_3	35·160	30·588
Er_2O_3	4·109	10·908
Ce_2O_3, La_2O_3, Di_2O_3	6·521	9·926
Be_2O_3	9·388	6·564
Fe_2O_3	2·150	—
FeO	12·401	16·040
CaO	1·106	0·787
MgO	traces	0·236
K_2O	—	traces
H_2O	2·321	0·620
	99·598	99·911

The specimen from Ytterby was much more easily decomposed by acids than that from Hitteröe, even cold hydrochloric acid sufficing for its decomposition. The high percentage of glucinum in the former, combined with the fact that this specimen was entirely without action upon polarised light, does not agree with Des Cloizeaux's hypothesis that the amorphous gadolinites are free, or nearly so, from glucinum.

The above experiments were mostly made in Professor Bunsen's laboratory, and we wish to express our hearty thanks for his continual help and guidance.

Addendum.—The above paper was written before the publication of the latest researches of MM. Marignac and Delafontaine.* Whether the new earths that have been announced by these chemists really exist in the crude yttria must still be a matter of doubt, particularly the "philippia" and "decipia" of M. Delafontaine, about which so few details are given. To decide whether the "ytterbia" and terbia of M. Marignac really exist, further experiments are necessary, with which we are at present engaged, and which will form the subject of another communication.

* See Abstracts, pp. 113—118.

XV.—*On the Formation of Barium Periodate.*

By S. Sugiura, Student in the Royal College of Chemistry, and C. F. Cross, Esq.

We stated in our last paper (September, 1878) that by passing iodine vapour, in a current of dry air, over the heated oxides of barium and calcium, basic periodates are formed. We are now in a position to elucidate this reaction by the following facts and observations.

It is well known that when barium iodate is heated to a high temperature, the following reaction occurs :—

$$5Ba(IO_3)_2 = Ba_5I_2O_{12} + 4I_2 + 9O_2,$$

We find, by recent experiments, that on heating the iodide in a current of dry air till no more iodine is given off, a residue of this same basic periodate is left, as the following analyses show :—

(*a.*) ·757 gram gave ·775 gram of $BaSO_4$ and ·308 AgI.

(*b.*) ·630 gram gave ·258 gram AgI.

	(*a.*)	(*b.*)	Calc. for $Ba_5I_2O_{12}$.
Ba	60·19	—	60·56
I.....	21·98	22·19	22·43
O	—	—	17·01
			100·00

Further, ·173 gram of the iodide, heated as described, yielded ·098 gram of the periodate, corresponding almost exactly with the equation :—

$$5BaI_2 + 6O_2 = Ba_5I_2O_{12} + 4I_2.$$

Both reactions lead us to the conclusion that this body is the expression of the most stable combination of the atoms of barium, iodine, and oxygen, and to the inference that it is also the product of the reaction of these elements in the experiments described in our previous communication; and this we have substantiated by qualitative experiments, indicating its identity with the periodate in question, which is established by the following analyses :—

(*a.*) The product of the action of iodine (in air) on BaO, ·458 gram gave ·3525 gram $BaSO_4$.

(*b.*) That of the action of oxygen on BaI_2, ·256 gram gave ·1985 gram $BaSO_4$.

	Calc. for $Ba_5I_4O_{19}$.	(*a*.)	(*b*.)
Ba	45·76	45·25	45·59*

In experiment (*a*) we avoided the use of either oxide of barium, as such, in favour of the carbonate,† with the object of entirely excluding water and preventing the occurrence of the reaction:—

$$6Ba(OH)_2 + 6I_2 = 5BaI_2 + Ba(IO_3)_2 + 6H_2O,$$

which by the further resolution of the iodide or iodate, would give rise to periodate. Now it was found that, on heating the carbonate in a tube exhausted of air and filled with the vapour of iodine, none of the latter entered into combination, but so soon as dry air was admitted the formation of periodate commenced. Hence we conclude that the formation of periodate, in the case observed by us, is referable *not* to the direct replacement of oxygen by iodine and the subsequent oxidation of iodide thus formed, but to the oxidation of iodine itself (a supply of nascent oxygen being determined by the presence of air and barium oxide), and the union of oxidised molecules with barium oxide.

Similar reactions we find to occur with strontium and calcium oxides, but in less marked degree, owing to the inferior stability of the products.

XVI.—*The Action of Alkaline Hypobromite on Oxamide, Urea, and Potassium Ferrocyanide.* Part II.

By William Foster, B.A., Lecturer on Chemistry, Middlesex Hospital Medical College.

The Action of Alkaline Hypobromite on Oxamide.

In my former paper on this subject (*Chem. Soc. J.*, October, 1878) I showed that when oxamide is agitated with a solution of alkaline hypobromite the mixture effervesces briskly, giving off gaseous nitrogen, and that 75 per cent. of the total nitrogen of the oxamide may be readily obtained in this way. I then showed that the greater portion of the remaining nitrogen could be obtained as ammonia by distilling

* Analysed after dissolving in nitric acid and reprecipitating by ammonia, the precipitate containing only one-half of the base originally present. Vide *Watts' Dic.*, vol. 3, 309.

† The carbonate has been shown by Lambert (*Compt. rend.*, 86, 332) to be dissociated on heating in a current of inert gas.

for several hours in presence of considerable quantities of the "copper-couple;" also that the alkaline oxamide residue, when strongly fused, gave the usual indications of nitrites. During the progress of my experiments, Mr. Fenton's first paper on the action of hypochlorite on urea was published (*Chem. Soc. J.*, July, 1878), in which he showed that one-half of the nitrogen of urea is converted into cyanate. During the interval between the reading and publication of Mr. Fenton's paper, I prepared some pure potassium cyanate, treated a known quantity with excess of hypobromite, and then distilled the whole with large quantity of the "copper-couple." Ammonia appeared in the distillate, and continued to come over after several hours' continued boiling, exactly in the same way as when the oxamide residue was similarly treated. This result was entirely unexpected. Search was now made for cyanate in the oxamide residue, and in this respect I was guided by the methods which Mr. Fenton had used so successfully in his experiments with hypochlorite on urea.

The perfectly clear yellow alkaline hypobromite solution containing the suppressed nitrogen from a quantity of oxamide, was then slowly added to pure hydrochloric acid in a flask, the amount of acid being more than sufficient to neutralise the whole of the alkali. Crystals of sodium sulphite were placed in the acid, and maintained in excess by adding fresh quantities from time to time. In this way the bromine set free on adding the hypobromite to the acid was removed as fast as it was liberated, and at the close of the operation the solution was distinctly acid, and contained free sulphurous acid. This latter was then completely evolved by boiling the mixture. The solution, devoid of free bromine and sulphurous acid, was then rendered alkaline with sodium hydrate solution, and Nessler's solution added, when a deep red colour was produced.

A fresh quantity of hypobromite solution, containing suppressed nitrogen from an oxamide experiment, was then diluted with several volumes of distilled water, and dilute nitric acid added very carefully until there was a faint indication of the presence of free bromine. Excess of silver nitrate solution was then added, and the bulky silver precipitate carefully washed with distilled water. The silver precipitate was digested with hydrochloric acid containing sodium sulphite, then boiled, diluted with distilled water, and filtered. On making the filtrate alkaline with sodium hydrate solution, and adding a few drops of Nessler's reagent, I obtained deep red colour.

The filtrate from the silver precipitate when treated with excess of acid, heated, made alkaline with sodium hydrate solution and Nessler's reagent added, gave but faint indications of ammonia in comparison with the foregoing.

A fresh portion of the hypobromite solution which had been treated

with oxamide was diluted, and acetic acid added until there was a slight excess. A few drops of a solution of calcium chloride were then added without producing the slightest turbidity. This shows entire absence of the oxalic acid radicle.

The above reactions being those of a cyanate, I infer that the whole of the suppressed nitrogen is in that condition, from the following quantitative experiments, the decomposition being expressed by the equation :—

$$4(NH_2)_2C_2O_2 + 15NaBrO + 18NaHO = 3N_2 + 2NaCNO + 8Na_2CO_3 + 15NaBr + 17H_2O.$$

Weighed quantities of oxamide were added to excess of the hypobromite solution, placed in a flask, and after the effervescence due to the escaping nitrogen had ceased, the solution was warmed. The bright yellow solution was then slowly added to pure hydrochloric acid, placed in a flask containing crystals of sodium sulphite, the acid and sulphite being maintained in excess until the whole of the hypobromite solution had been added. The temperature of the mixture rises very considerably during the operation, and the solution being distinctly acid, the application of external heat for a short time suffices to expel the whole of the excess of sulphurous anhydride. The acid solution was then rendered alkaline by solution of sodium hydrate, and its volume either determined, or made up to a known volume as small as possible. This latter method I have adopted for convenience. A fraction of this total volume was then taken and treated with excess of fresh alkaline hypobromite, the evolved nitrogen being collected and measured as in ordinary cases. The following are the last two of numerous experiments in this direction :—

Oxamide taken in grams.	c.c. of nitrogen obtained uncorrected.	Percentage of nitrogen obtained.	Amount of suppressed nitrogen to be accounted for.
·692	46·0	7·73	—
·750	50·0	7·84	7·95

Oxamide contains 31·8 per cent. of nitrogen.

Some of my earlier experiments gave from 9 to 10 per cent. of nitrogen by this method—one ill adapted for quantitative purposes with the apparatus I have employed. The different processes necessitate considerable dilution of the solution, and this being loaded with alkaline salts, it is not advisable to concentrate it. Taking but a fraction of such solution, the yield of gas is very small, in which case the

error of experiment is apt to be something considerable. Another source of error was due to attempts to dissolve relatively large quantities of oxamide in small quantities of strong hypobromite solution. In such cases the oxamide disappears with some difficulty, the remaining particles no doubt giving the total nitrogen they contain when treated as above.

The Action of Alkaline Hypobromite on Urea.

In my former experiments I showed that when urea is treated with alkaline hypobromite of the normal strength, 92 per cent. of the total nitrogen can be obtained in the gaseous state; that when stronger alkaline solutions are employed, the yield of gas may be increased; but that results obtained by means of such viscid solutions are probably slightly inaccurate. All observers are agreed as to there being a deficiency of nitrogen, and some have suggested that it is caused by the spirting of the mixture when the urea and hypobromite solutions come in contact, the deficiency being diminished, but not altogether avoided, by passing the nitrogen through fresh quantities of alkaline hypobromite.

Thinking it possible that some of the nitrogen might escape as ammonia, urea and hypobromite solutions were slowly mixed in a test-tube, after a plug with delivery-tube had been inserted. The escaping nitrogen was made to pass through pure dilute hydrochloric acid. On adding sodium hydrate in excess to the acid, and testing with Nessler's solution, negative results were always obtained.

Some urea solution was then added to alkaline hypobromite solution, the latter being in excess, and after the effervescence had ceased the solution was warmed. The bright yellow solution obtained was added to an excess of pure hydrochloric acid containing crystals of sodium sulphite (taking the precautions mentioned in connection with oxamide experiments), and eventually adding excess of solution of sodium hydrate and a few drops of Nessler's solution. A very marked coloration was always obtained.

The amount of nitrogen recoverable as ammonia by this method was determined. 0·886 gram of urea was dissolved in water and added to excess of alkaline hypobromite of about the normal strength. When the effervescence had ceased, heat was applied to the flask until the solution had a bright yellow colour. This solution was added to excess of hydrochloric acid containing sodium sulphite, warmed, sodium hydrate solution added in excess, and distilled. The ammonia coming over was received in a vessel containing dilute hydrochloric acid, and afterwards converted into platinum-ammonium chloride. The amount obtained was 0·497, and is equal to 0·031 of nitrogen.

The total amount of nitrogen in the quantity of urea taken is 0·413, and expressing the ratio of the quantity of nitrogen obtained to this total quantity as a percentage, we get 7·5, a number which agrees very closely with that representing the amount of nitrogen suppressed in urea determinations. From these experiments I infer that this percentage of the total quantity is wholly converted into cyanate in such determinations.

The Action of Alkaline Hypobromite on Potassium Ferrocyanide.

When this salt in aqueous solution is added to the alkaline hypobromite solution, there is no apparent action at ordinary temperatures. If the mixture be heated, its appearance does not alter in any marked degree until the temperature rises to about 90° C., when it deepens in colour, appearing almost black by reflected light. At about 95° effervescence fairly commences, and by the time that the mixture reaches the boiling point it is tolerably active. If the source of heat be removed and the mixture allowed to remain at rest, a dark-coloured precipitate subsides, whilst the bright solution has a deep claret-red colour when seen by transmitted light. This colour changes to violet on dilution with water. On adding the red liquid to excess of hydrochloric acid containing sodium sulphite, then making alkaline with excess of sodium hydrate solution and warming, the odour of ammonia is very distinct.

My earliest experiments were made with about 0·6 gram of ferrocyanide dissolved in a small quantity of water and added to about 40 c.c. of normal alkaline hypobromite solution. I have found that such a mixture requires to be kept at the boiling temperature for about 15 minutes in order to effect perfect decomposition of the ferrocyanide. Assuming the gas evolved during the operation performed in this way to be pure nitrogen (I have subsequently found that it is not), the quantity obtained is (speaking roughly) about one-half the total quantity present in the amount of ferrocyanide used. On adding this alkaline solution to excess of hydrochloric acid containing sodium sulphite, distilling with excess of sodium hydrate solution, collecting the evolved ammonia, and estimating the nitrogen as the double platinum salt, I always found more than was required by theory, supposing the whole of the gas obtained in the first part of the experiment to be pure nitrogen. This led me to examine the deep-red liquid which has been alluded to. Without describing details, I may state that when it was boiled, I found it was capable of yielding gaseous oxygen. It has the appearance and leading properties of sodium ferrate. I intend examining it more fully. Other simpler methods of obtaining it have been observed.

Having discovered that the nitrogen coming off at the boiling point was apt to be contaminated with oxygen, I then boiled weighed quantities of ferrocyanide with excess of alkaline hypobromite in open vessels until the whole of the ferrocyanide had disappeared, disregarding the character and amount of the gas evolved. The solution was then added to excess of hydrochloric acid, and the amount of ammonia so produced was distilled, the nitrogen being estimated as the platinum-ammonium salt. Variable results have been obtained by this method, the average of several experiments representing the suppressed nitrogen as 13 per cent. Ferrocyanide contains 19·9 per cent. of nitrogen.

It would appear from the experiments I have made that about one-third of the total nitrogen of the ferrocyanide is evolved as gas during the interval necessary for completing the decomposition of the ferrocyanide, the remaining nitrogen being oxidised into cyanate, which, at the temperature employed, slowly yields gaseous nitrogen, in consequence of secondary actions due to the presence of the iron compound. By boiling the mixture for an hour, the amount of nitrogen susceptible of conversion into an ammonium salt by excess of mineral acid is considerably diminished. In one experiment I obtained 5·5 per cent. of nitrogen from the ferrocyanide used.

Dr. Russell has suggested the use of weaker alkaline solutions and lower temperatures, which, though they may suffice for the oxidation of the cyanogen of the ferrocyanide, would not be high enough to bring about secondary actions between the cyanate and ferrate. I am at present working in this direction.

I may mention that cyanides, such as potassium cyanide, when heated with the alkaline hypobromite, are oxidised into cyanate, but as my experiments on the behaviour of pure potassium cyanate are not quite complete, I have deferred bringing them forward.

I have also partially investigated the action of alkaline hypobromite on acetamide and benzamide. The former begins to be attacked at 80°, but yields only a portion of its nitrogen in the gaseous state. Benzamide is also perfectly stable until high temperatures are reached.

I am very desirous of ascertaining the behaviour of cyanamide, but have hitherto been prevented by the difficulty in obtaining it.

XVII.—*The Derivatives of Di-isobutyl.*

By W. Carleton-Williams, Assistant Lecturer on Chemistry, The Owens College.

The di-isobutyl used in these experiments was prepared by the action of sodium on isobutyl bromide, as described in my previous communication to the Society (this Journal, 1877, **1**, 541). It was carefully purified by being left in contact with strong sulphuric acid for several hours, and was afterwards treated with a mixture of concentrated sulphuric and nitric acids, then washed with water, and allowed to stand over solid caustic potash two or three days. It was finally dried over sodium, and subjected to fractional distillation. 10 pounds of isobutyl bromide yielded about 1 litre of the purified hydrocarbon boiling between 106° and 110°.

In order to determine the specific gravity of di-isobutyl, a slightly modified arrangement of Hannay's apparatus (this Journal, 1874, 203) was used, having a capacity of about 15 c.c. The following numbers were obtained, water at its maximum density being taken as unity:—

t.	Sp. gr.	*t*.	Sp. gr.
0°	0·7091	30°	0·686
0°	0·7085	40°	0·677
10°	0·7015	50°	0·669
20°	0·6931	100°	0·626

The pure hydrocarbon boils* at 108—108·3°, under a barometric pressure of 745 mm. (reduced to 0°), and remains liquid at −17°. These results agree closely with those obtained by Kopp (*Ann. Chem.*, **95**, 335), who found that di-isobutyl boils at 108·5° (cor.) under 747·5 mm. pressure, and has a specific gravity of 0·7135 at 0°, and 0·7001 at 16·4°.

The vapour-density of di-isobutyl was determined by Victor Meyer's process (*Deut. Chem. Ges. Ber.*, **10**, 2068), in which the volume occupied by the vapour of a known weight of substance is measured by the weight of mercury expelled. This method is expeditious, yields accurate results, does not involve the use of a large quantity of mercury (not more than 40 c.c. being required), and the apparatus is very simple.

In the following experiments S = the weight of substance, T = temperature of the vapour; *t* = temperature of the atmosphere;

* In determining the boiling points given in this paper, the column of mercury in the thermometer was completely immersed in the vapour of the boiling liquid.

P = the barometric pressure; p = the height of the column of mercury in the apparatus at the end of the experiment, s = tension of vapour of mercury at the temperature T; a = weight of mercury taken; r = weight of mercury remaining in the apparatus at the end of the experiment; and q = weight of mercury required to fill the Hofmann's bottle.

In two determinations of the vapour-density of di-isobutyl, P = 765 mm., p = 35 mm., s = 2·17 mm., t = 15°, T = 129°, q = 1·17 grams.

In Exp. I. .. S = 0·0413 grm. a = 230·77 grms. r = 82·32 grms.
In Exp. II... S = 0·0407 „ a = 230·57 „ r = 86·07 „

Experiment.		Calculated for
I.	II.	C_8H_{18}.
57·64	58·51	57

An examination of the refractive power of di-isobutyl gave the following results:—

	Potassium (red line).	Lithium.	Sodium.	Thallium.	Strontium (blue line).
Refractive indices at 16° = μ	1·3901	1·3917	1·3943	1·396	1·4008
Refractive energy $\frac{\mu-1}{d}$ ..... d = 0·6972 at 16°	0·5591	0·5618	0·5655	0·568	0·5748
Refraction equivalent, $\frac{P\mu-1}{d}$	63·78	64·04	64·47	64·75	65·55

On the assumption that C = 5 and H = 1·3, the calculated refraction equivalent for di-isobutyl is 63·4.

Di-isobutyl has no action on polarised light.

A mixture of primary and secondary chlorides is obtained when the hydrocarbon is chlorinated by Schorlemmer's method (*Phil. Trans.*, 1872, 122), which consists of passing a current of dry chlorine into the vapour of boiling di-isobutyl (instead of into the liquid) in the presence of diffused sunlight. The chlorinated product remains liquid at −17°, and has no constant boiling point. The iso-primary and iso-secondary chlorides cannot be separated even by repeated fractional distillation.

The acetates were prepared by heating the mixed chlorides with glacial acetic acid and potassium acetate to 200° for twelve hours; at the end of this time the greater part of the chlorides had disappeared, but considerable difficulty was experienced in decomposing the last traces. The olefine or mixture of olefines formed at the same time as the acetates appears to be chiefly, if not entirely, derived from

the decomposition of the secondary chloride. The examination of this substance will form the subject of a future research.

The mixture of iso-primary and iso-secondary acetates does not solidify at −17°. It boils between 170° and 205°, but it could not be separated by fractional distillation. The acetates were converted into alcohols in the usual way, by boiling with a concentrated solution of caustic potash. After numerous distillations I succeeded in separating the primary from the secondary alcohol.

The Alcohols.

The iso-primary alcohol, $C_8H_{17}.OH$, has a pleasant orange-like odour, and a hot burning taste. It remains liquid at −17°, and boils at 179—180° under 765 mm. pressure (not reduced). It dissolves in alcohol, ether, and chloroform, and is sparingly soluble in water. The addition of water to the alcoholic solution causes the substance to separate out.

The specific gravity of the alcohol compared with water at 4°, was determined at the following temperatures:—

0°	0·841	40°	0·814
12°	0·833	50°	0·807
20°	0·828	100°	0·767
30°	0·821		

A determination of the vapour-density of this alcohol gave the following results:—S = 0·0485 gram, a = 321·07 grams, r = 113·52 grams, q = 1·17 grams, P = 761·1 mm. (reduced to 0°), p = −19 mm., s = 28·5 mm., t = 15°, and T = 215°.

	Experiment.	Theory.
Vapour-density of $C_8H_{18}O$.....	66·02	65·0

Analysis.—0·2157 gram of substance formed, on combustion with copper oxide in a current of oxygen, 0·5802 gram of CO_2 and 0·2667 gram of H_2O.

	Found.	Calculated for $C_8H_{18}O$.
C	73·36	73·84
H	13·73	13·84
O	—	12·32

The iso-secondary alcohol is not only obtained in much smaller quantities than its isomeride (for reasons previously mentioned), but it is also much more difficult to separate from traces of undecomposed chloride. It boils at 160—163° under 755 mm. pressure, and remains liquid at −17°. This alcohol differs from the iso-primary by having a fainter smell, a lower specific gravity, and a larger coefficient of

expansion. The specific gravity of the alcohol was taken at the following temperatures:—

15°	0·820	40°	1·801
30°	0·811	50°	0·793

The determination of the vapour-density gave the following results:—S = 0·0481 gram, a = 322·89 grams, r = 128·39 grams, q = 1·17 grams, P = 768·6 mm. (reduced to 0°), p = −30 mm., s = 11, t = 16°, and T = 180°.

	Experiment.	Theory.
Vapour-density of $C_8H_{18}O$.....	65·38	65·0

The iso-octoic acid, $C_8H_{16}O_2$, prepared by oxidising the iso-primary alcohol with a cold dilute mixture of potassium bichromate and sulphuric acid, is an oily liquid, which boils at 218—220° under 767 mm. pressure (reduced), and does not solidify at − 17°. It is soluble in alcohol and in ether, and is sparingly soluble in water; 100 c.c. of water at 15° dissolve 0·15 gram of the acid. At the ordinary temperature the acid possesses an unpleasant odour, which becomes much more powerful at higher temperatures, when it somewhat resembles rotten cheese. The specific gravity of the acid compared with water at 4° is—

At 0°.....	0·926	40°	0·893
„ 20°.....	0·911	50°	0·885
„ 30°.....	0·903	100°	0·846

In addition to the silver, barium, and calcium salts, which have been previously described (this Journal, 1877, 543), the following iso-octoates were prepared:—

The *sodium* salt, obtained by neutralising the acid with sodium carbonate and evaporating the liquid over sulphuric acid at the ordinary temperature, is a deliquescent gum-like mass, which begins to show signs of crystallisation after standing for several days *in vacuo* over sulphuric acid.

Potassium Iso-octoate forms a semi-crystalline deliquescent mass. Its aqueous solution produces with silver nitrate a white precipitate, which after crystallisation from hot water, in which it is not very soluble, gave the following results:—

	Calculated for $C_8H_{15}AgO_2$.
0·478 gram gave 0·207 Ag = 43·30 p. c. Ag.	—
0·0702 „ „ 0·0305 Ag = 43·34 p. c. Ag.	43·03 p. c. Ag.

The concentrated solution of the potassium salt produces in a solution of mercuric chloride a faint turbidity; with mercuric nitrate no precipitate; with mercurous nitrate a dense white precipitate, which is soluble in hot water and crystallises out again on cooling. Lead

acetate and manganese nitrate form amorphous precipitates insoluble in water. Cupric acetate throws down a green precipitate, insoluble in water, but soluble in alcohol, forming a green solution, from which the copper salt is deposited in minute green plates, which are generally arranged together in pyramidal clusters.

Magnesium Iso-octoate, $Mg(C_8H_{15}O_2)_2 + 2H_2O$, prepared by dissolving magnesia in the acid, forms a transparent, deliquescent, non-crystalline mass, which slowly becomes opaque and crystalline when left in a vacuum over sulphuric acid.

0·2058 gram gave 0·0505 $MgCO_3$ and 0·022 H_2O.

	Found.	Calculated for $Mg(C_8H_{15}O_2)_2 + 2H_2O$.
Mg	7·01	6·86
H_2O	10·70	10·30

The *zinc salt* obtained by dissolving zinc carbonate in the acid, forms a white pearly mass, which is decomposed by water, but dissolves in dilute iso-octoic acid.

Strontium Iso-octoate is precipitated when concentrated solutions of strontium nitrate and potassium iso-octoate are mixed together. The precipitate dissolves freely in absolute alcohol, and is deposited from the alcoholic solution in transparent six-sided plates, which appear to belong to the monoclinic system, and to consist of a combination of the basal terminal plane with the clinodiagonal and orthodiagonal domes. This substance is slightly less soluble in hot than in cold water. When a solution saturated at the ordinary temperature is heated, it becomes slightly turbid. The salt is deposited from an aqueous solution in transparent needle-shaped crystals, which effloresce and grow opaque on exposure to the air. Strontium iso-octoate was also prepared by neutralising iso-octoic acid with a solution of strontia.

The *ethyl ether* of iso-octoic acid is obtained by saturating an alcoholic solution of the acid with hydrochloric acid gas, adding water to the product, and washing with a dilute solution of caustic soda. The ether is lighter than water, boils at about 175°, and possesses a powerful and characteristic odour.

The determination of the vapour-density of the ether gave the following results:—S = 0·0492 gram, a = 320·62 grams, r = 143·15 grams, q = 0·89 gram, P = 758·1 mm. (reduced), p = −36 mm., s = 28·5, T = 215°, and t = 14°.

	Experiment.	Calculated for $C_8H_{15}O_2.C_2H_5$.
Vapour-density	84·39	86

Di-isobutyl Iso-octoate, $C_8H_{15}O_2.C_8H_{17}$, is formed in small quantities

in the preparation of iso-octoic acid by oxidising the primary alcohol. It is a colourless liquid, which boils at 278—281°, and is lighter than water. It is slowly saponified by heating with alcoholic potash at 120° in sealed tubes.

The *ketone*, $C_8H_{16}O$, which is formed when the secondary alcohol is oxidised by a cold dilute mixture of sulphuric acid and potassium bichromate, boils at 159—161° under 743·2 mm. pressure, and has a specific gravity of 0·865 at 14°. The ketone remains liquid at −17°, and does not form a crystalline compound with acid sodium sulphite. The chief product of the oxidation of the ketone is acetic acid; a small quantity of a higher acid, probably isobutyric, is also formed; but as I expect shortly to obtain larger quantities of the secondary alcohol and ketone, in the course of a research on the action of bromine on di-isobutyl, I shall postpone the detailed account of these oxidation-products to my next communication.

XVIII.—*On Stannic Ethide.*

By E. Frankland, F.R.S., and Awbrey Lawrance, Esq.

In the year 1852 the existence of the organo-compounds of tin was announced by one of us (*Phil. Trans.*, **142**, 418), the reduction of organo-stannic to organo-stannous compounds was described, and stannous ethide was prepared by the action of zinc upon an aqueous solution of stannic diethochloride:—

$$\mathbf{Sn}Et_2Cl_2 + Zn = \mathbf{Zn}Cl_2 + \mathbf{Sn}Et_2.$$

The preparation of large quantities of stannous ethide by this method, however, is extremely difficult; because, as the reaction progresses, the product gradually undergoes spontaneous decomposition into metallic tin and stannic ethide:—

$$2\mathbf{Sn}Et_2 = Sn + \mathbf{Sn}Et_4.$$

In order to obtain stannous ethide more quickly, so as to reduce the spontaneous decomposition to a minimum, we endeavoured to prepare it by the action of zinc-ethyl upon dry stannous chloride. In this, however, we were disappointed, but the method turned out to be much superior to any previously known for obtaining stannic ethide in large quantities: for since the reaction, which was attended from the first by the separation of much spongy tin, obviously proceeded as indicated by the following equation, being exactly analogous to that observed in the formation of plumbic ethide, which will be described by us in a subsequent paper.

$$2\mathbf{Sn}Cl_2 + 4\mathbf{Zn}Et_2 = Sn + \mathbf{Sn}Et_4 + 4\mathbf{Zn}EtCl.$$

This reaction is much less violent, and therefore more under control than that of Buckton (*Phil. Trans.*, 1859, page 424), in which stannic chloride and zinc-ethyl were employed. The anhydrous stannous chloride was obtained by heating commercial stannous chloride until most of its water of crystallisation was expelled, and then fusing the resulting mass in a Hessian crucible. The melted chloride was poured out in a thin layer upon an iron slab, and then broken into fragments, which were afterwards carefully preserved from moisture.

To prepare stannic ethide, it is only necessary to add these fragments of the fused chloride to zinc-ethyl contained in a flask or retort, avoiding excess of the chloride; too great an elevation of temperature should be prevented by placing the vessel in cold water. As soon as the mixture ceases to fume in the air when a little of it is exposed on the end of a glass rod, sufficient of the chloride has been added. If more were used, the product would be contaminated with ethochlorine compounds of tin, which are easily recognised by their pungent odour.

The pasty mass must now be distilled in an oil-bath until everything volatile has passed over. The distillate, which ought to contain some free zinc-ethyl, is to be poured into water, the white precipitate of zincic hydrate dissolved by dilute sulphuric acid, and the heavy oily layer of crude stannic ethide separated. The latter is repeatedly washed with water, then dried over calcic chloride, and finally rectified. In addition to the known properties of stannic ethide (*Phil. Trans.*, 1859, page 424—425), we have to mention the following:—Stannic ethide has no action upon aluminium, sodium, or magnesium up to a temperature of 180° C. It seems to have a slight action upon benzoic aldehyde, but it has none upon acetone or ethylic oxalate when it is heated with these bodies to 180°. It remains unchanged after prolonged exposure, at ordinary temperatures, to the following gases:—Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen. Stannic ethide, however, slowly absorbs sulphurous anhydride with the formation of ethylsulphonic and ethoxystannic compounds.

Action of Sulphurous Anhydride upon Stannic Ethide.

Sulphurous anhydride was continuously supplied to a large glass bottle containing several ounces of stannic ethide. As the absorption of the gas progressed, the stannic ethide assumed first a light, and afterwards a darker yellow colour, and a syrupy consistency. The liquid was frequently made to flow round the sides of the bottle, so as to expose a larger surface to the gas. At the end of several weeks, an abundant crop of acicular crystals was formed, but there was also a

considerable quantity of an uncrystallisable yellow liquid remaining, which refused to absorb more of the gas.

Preliminary experiments showed that the oily liquid was soluble in ether, whilst the crystals were nearly insoluble. The liquid was therefore drained from the crystals, and the latter were then washed with ether until they were freed from the adhering oil. The crystalline powder which remained at the end of this operation was placed over sulphuric acid in a vacuum, and then submitted to analysis, with the following results:—

I. ·1850 gram burnt with cupric oxide gave ·1879 gram of carbonic anhydride, and ·0994 gram water.

II. ·4586 gram treated with fuming nitric acid, evaporated to dryness and ignited, gave ·2757 gram stannic oxide.

III. ·3378 gram dissolved in alcohol, diluted with water and precipitated by baric chloride, gave ·1592 gram of baric sulphate.

These numbers agree well with those calculated from the formula of stantriethylic sulphate,

$$SO_2(SnEt_3O)_2,$$

as is seen from the following comparison:—

	Calculated.		Found.
C_{12}	144	28·46	27·70
H_{20}	30	5·93	5·96
Sn_2	236	46·65	47·29
S	32	6·32	6·45
O_4	64	12·64	12·60
	506	100·00	100·00

This compound is the sulphate of sesquistanethyl described by Cahours (*Ann. Chim. Phys.* [3], **58**, 55) and Buckton (*Phil. Trans.*, 1859, page 428), and to their description of its properties we have nothing to add.

The oily liquid and the residues obtained from the washings with ether were dissolved in alcohol, the solution was largely diluted with water, solid baric hydrate added, and the mixture allowed to stand for some time. The liquid was then filtered, and the strongly alkaline filtrate distilled until about two-thirds had passed over. The distillate was strongly alkaline, indicating the presence of a volatile organo-tin base which, from its peculiar odour of horse-radish, was judged to be stantriethylic hydrate—a supposition which was confirmed by the copious separation of fine needles when acetic acid was added to the distillate, tristanethylic acetate being, according to Cahours (*Ann. Chim. Phys.* [3], **58**, 57), nearly insoluble in water. Acetic acid was added to the distillate so long as the sparingly soluble acetate con-

tinued to be formed, and the crystalline precipitate was washed repeatedly with cold water. A further quantity of the crystals was obtained by evaporating the washings *in vacuo*. When evaporated on the water-bath, the acetate sublimes with the steam. The crystalline precipitate on the filter was dissolved in alcohol, the solution evaporated *in vacuo*, and the fibrous mass thus obtained submitted to analysis with the following results:—

I. ·1670 gram burnt with cupric oxide gave ·2184 gram of carbonic anhydride and ·1028 gram water.

II. ·1335 gram, treated with strong nitric acid and ignited, gave ·0760 gram stannic oxide.

These numbers agree well with the formula of stantriethylic acetate:—

$$C_8H_{18}SnO_2, \text{ or } \begin{cases} CH_3 \\ CO(SnEt_3O) \end{cases}$$

as is seen from the following comparison:—

	Calculated.		Found.
C_8	96	36·36	35·66
H_{18}	18	6·81	6·84
Sn.....	118	44·70	44·78
O_2	32	12·13	12·72
	264	100·00	100·00

To ascertain the composition of the acid with which the volatile organo-tin base was combined in the original oily liquid, carbonic anhydride was passed through the alkaline residue in the retort from which the organo-tin base had been distilled until the excess of baryta was precipitated; the liquid was then boiled, filtered, and the filtrate evaporated to dryness. The crystalline residue thus obtained was the barium salt of ethylsulphonic acid (SO_2EtHo), for on analysis it yielded the following results:—

I. 0·2096 gram burnt with cupric oxide gave 0·1049 gram of carbonic anhydride and 0·0606 gram of water.

II. 0·1852 gram burnt with potassic chlorate and sodic carbonate, and precipitated by baric chloride, gave 0·2540 gram of baric sulphate.

III. 0·1450 gram treated with sulphuric acid, and ignited, gave 0·0941 gram of baric sulphate.

Calculated into percentages, these numbers agree with those required for baric ethosulphate,

$$\begin{matrix} SO_2Et \\ SO_2Et \end{matrix} BaO'''$$

as is shown by the following comparison:—

	Calculated.		I.	II.	III.
C_4	48	13·52	13·66	—	—
H_{10}	10	2·82	3·21	—	—
S_2	64	18·03	—	18·84	—
Ba	137	38·59	—	—	38·14
O_6	96	27·04	—	—	—
	355	100·00			

We believe the following to be the explanation of the reaction between sulphurous anhydride and stannic ethide, resulting in the formation of stantriethylic sulphate and ethylsulphonate, the conditions of the experiment having been such as to allow the continual admission of atmospheric air into the vessel in which the reaction was performed. The fundamental reaction consists in the transformation of stannic ethide and sulphurous anhydride, in the presence of oxygen, into stantriethylic ethylsulphonate, according to the following equation:—

$$\underset{\text{Stannic ethide.}}{SnEt_4} + SO_2 + O = \underset{\text{Stantriethylic ethylsulphonate.}}{SO_2Et(SnEt_3O)}$$

After, and possibly also during, this reaction, some of the sulphurous anhydride becomes converted into sulphuric acid, expelling ethylsulphonic acid from the oily compound, and forming the crystalline stantriethylic sulphate according to the following equation:—

$$\underset{\text{Stantriethylic ethylsulphonate.}}{2SO_2Et(SnEt_3O)} + \underset{\text{Sulphuric acid.}}{SO_2Ho_2} = \underset{\text{Stantriethylic sulphate.}}{SO_2(SnEt_3O)_2} + \underset{\text{Ethylsulphonic acid.}}{2SO_2EtHo.}$$

The appearance of the crystals only after the reaction had progressed for several weeks confirms this explanation; it is obvious, however, that if it is correct, neither stantriethylic sulphate nor ethylsulphonate could be formed if atmospheric air were excluded during the reaction, but although we repeated the operation with the strict observance of this new condition, we have not been able to prevent the formation of these bodies.

Action of Sulphurous Anhydride upon Stannic Ethide out of Contact with Air.

Several ounces of stannic ethide were introduced into a flask filled with mercury, and inverted in a mercury trough; dry sulphurous anhydride was then passed into the flask when required. As in the previous operation, the absorption was slow and required about six weeks for its completion. The limpid stannic ethide gradually became

thick and black, owing to the deposition of spongy metallic tin, whilst the mercury became alloyed with this metal. No crystalline body appeared to form. The black mass was treated with water in which it was, for the most part, soluble; the solution was filtered, and the filtrate evaporated upon a water-bath. In this way a crystalline mass was obtained, which, as analysis showed it to be a mixture, was redissolved in water, treated with excess of caustic baryta, and submitted to distillation.

The distillate was found to give an alkaline reaction, and on addition of acetic acid, it gave the characteristic precipitate of sesquistanethylic acetate.

The residue in the retort was filtered, the insoluble portion being found to consist of nearly pure baric sulphate. Carbonic anhydride was passed through the filtrate to remove excess of baryta; the solution was boiled and filtered, and the filtrate concentrated to its crystallising point. Colourless rhomboidal plates were thus obtained, which, on analysis, gave the following results:—

I. 0·5230 gram of these crystals well pressed between filter-paper lost ·0352 gram when dried in the steam oven, which is equivalent to 6·73 per cent. of water.

II. 0·2403 gram of the dried substance, when burnt with sodic carbonate and potassic chlorate, and subsequently precipitated by baric chloride, gave 0·3313 gram of baric sulphate.

III. 0·1663 gram of the dried substance gave, when ignited with sulphuric acid, 0·1088 gram of baric sulphate.

IV. 0·1633 gram of the dried substance gave 0·0508 gram of water and 0·0803 gram of carbonic anhydride.

These numbers agree with those required by baric ethylsulphonate, as the following comparison shows:—

	Calculated.		II.	III.	IV.
C_4	48	13·52	—	—	13·41
H_{10}	10	2·82	—	—	3·45
S_2	64	18·03	—	18·93	—
Ba	137	38·59	38·47	—	—
O_6	96	27·04	—	—	—
	355	100·00			

Notwithstanding the exclusion of air during the reaction, the final products were the same as in the first case, viz.:—Stantriethylic sulphate and stantriethylic ethylsulphonate, whence we infer that oxidation occurred during the solution and evaporation of the products.

Shortly summarised, the experiments detailed in this paper establish:—

1. That stannic ethide can be most conveniently prepared by the action of zinc-ethyl upon stannous chloride.

2. That stannic ethide is not acted upon at 180° by aluminium, sodium, or magnesium.

3. That no chemical change takes place when stannic ethide is heated to 180° in contact with acetone or ethylic oxalate.

4. That stannic ethide undergoes no change by prolonged exposure to the following gases:—Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen,* sulphuretted hydrogen.

5. That stannic ethide slowly absorbs sulphurous anhydride.

6. That when atmospheric air is present, there are formed in the last case a transparent oily body and a crystalline compound.

7. That the oily body consists chiefly of stantriethylic ethylsulphonate, $SO_2Et(SnEt_3O)$.

8. That the crystalline compound is stantriethylic sulphate, $SO_2(SnEt_3O)_2$.

XIX. *On the Action of Isobutyric Anhydride on the Aromatic Aldehydes.*

By W. H. Perkin, F.R.S.

When an aromatic aldehyde is heated with normal butyric anhydride and a butyrate, an angelic acid is obtained containing the hydrocarbon radicle of the aldehyde employed. Thus benzoic aldehyde yields phenylangelic acid and cuminic aldehyde cumenylangelic acid. It was therefore thought desirable to make further experiments in this direction, using isobutyric anhydride in place of the normal compound. These experiments led to the following results.

A mixture of cuminic aldehyde, isobutyric anhydride and sodium isobutyrate was heated in sealed tubes to about 150° for twenty-four hours. The resulting product when cool was amber-coloured and viscid, and on opening the tubes, frothed up very much, large quantities of carbonic anhydride escaping. It was mixed with water and boiled in a retort until the distillate was nearly free from oily matter. After cooling, the aqueous portion, consisting of sodium isobutyrate, was poured off from the thick oily product with which it was associated. The latter was then boiled with an excess of a solu-

* As stannic ethide always deposits a copious white precipitate after being kept for several years in stoppered bottles, it probably undergoes a very slow oxidation.

tion of sodium carbonate, and the insoluble oil removed. The boiling alkaline solution, on being acidified, deposited a thick oily acid, becoming a sticky mass on cooling. This was collected and dissolved in petroleum spirit, and after standing for several days, the solution deposited a quantity of oblique crystals. These were separated from the mother-liquors, pressed and recrystallised several times from the same solvent. They fused at 80°. On analysis they gave the following numbers:—

I. ·2342 of substance gave—

·6412 of CO_2 = 74·85 p. c. of carbon.
·1718 of H_2O = 8·15 p. c. of hydrogen.

II. ·2337 of substance gave—

·6396 of CO_2 = 74·62 p. c. of carbon.
·1770 of H_2O = 8·43 p. c. of hydrogen.

No. II was crystallised about six times.

After recrystallising specimens of the above eight or ten times from petroleum spirit, two sorts of crystals were deposited, one being the original product, the other large well-defined crystals of some other body. These were separated mechanically, and the latter recrystallised several times. On analysis, they gave the following numbers. Its fusing point was 91°:—

III. ·2158 of substance gave—

·6054 of CO_2 = 76·5 p. c. of carbon.
·1554 of H_2O = 8·00 p. c. of hydrogen.

A quantity of the acid first analysed, and fusing at 80°, was heated until it commenced to boil, an acid was volatilised having the odour of isobutyric acid. The residue was purified by conversion into the sodium salt and precipitation by hydrochloric acid. It was then crystallised, and gave on analysis the following numbers. It fused at 91°:—

IV. ·2176 of substance gave—

·6110 of CO_2 = 76·56 p. c. of carbon.
·1518 of H_2O = 7·75 p. c. of hydrogen.

The products used in analyses III and IV were evidently cumenylcrotonic acid, which required 76·5 per cent. of carbon and 7·87 of hydrogen, and fuses at 90—91°. That used in analyses I and II is apparently a compound of cumenylcrotonic acid with isobutyric acid, a substance of the composition $4(C_{13}H_{16}O_2)C_4H_8O_2$ would require 74·3 per cent. of carbon and 7·9 per cent. of hydrogen.

On making similar experiments with benzoic aldehyde, phenylcrotonic acid was used.

The isobutyric anhydride used in these operations was prepared with considerable care; nevertheless it was thought that the formation of the crotonic acids might be due to the presence of propionic anhydride. A quantity of isobutyric acid was therefore carefully and repeatedly fractioned, and fresh anhydride prepared from it. This was also fractioned. On using this, it was found that it yielded with cuminic and benzoic aldehydes a much smaller quantity of the crotonic acids, so that the formation of these compounds would appear to be due to propionic anhydride in the isobutyric anhydride. Under all circumstances, however, small quantities of uncrystallisable acids are produced, but up to the present time these have not been obtained in a fit state for analysis.

I have mentioned, in describing the foregoing experiments, that large quantities of carbonic anhydride escaped when the sealed tubes were opened. It was thought desirable to determine roughly the amount of this, and also to examine the oily fluids which pass over when the contents of these tubes are distilled with water.

β-Butenylbenzene.

Twenty grams of benzoyl hydride, thirty of isobutyric anhydride, and fifteen of sodium isobutyrate were heated together in a retort, the neck of which was raised, a condensing tube being attached to it, and to this an apparatus for the absorption of carbonic anhydride. When the temperature of the mixture had reached about 140°, carbonic anhydride began to form, and when it had reached 150°, the gas was evolved very rapidly, the temperature then gradually rose, until in the course of two or three hours, it reached about 180°. The amount of carbonic anhydride given off in this experiment amounted to 4·58 grams. In a second experiment it was 4·75 grams.

The product left in the retort was distilled with water until oily matter ceased to come over. The oily part of the distillate was then washed with alkali to remove isobutyric acid, and when separated from the alkaline fluid, distilled with solid potassium hydrate, and then several times with sodium. The potassium hydrate and also the sodium at first caused a brown substance to form in the oily product. When this was no longer produced, the oil was fractioned, that part boiling between 184—187° being kept separate. This constituted the principal part of the distillate. On analysis, however, it was found to contain a little oxygen, probably due to a trace of benzylic alcohol formed by the action of the caustic alkali upon benzoic aldehyde in the crude product. It was therefore shaken with a solution of potassium permanganate and potassium hydrate, and then after being dried and distilled over sodium, it gave the following numbers:—

·1716 of substance gave—

·5695 of CO_2, and

·1395 of H_2O.

	Theory for $C_{10}H_{12}$.	Experiment.
Carbon	90·9	90·5
Hydrogen	9·09	9·03

This hydrocarbon has therefore the composition of butenylbenzene, but curiously it is not identical with that obtained from phenylangelic acid (*Jour. Chem. Soc.*, 1877, **2**, 667). I therefore propose to call it *β-butenylbenzene*. Its boiling point is 184—186°, or nearly two degrees lower than that of the butenylbenzene already described. When oxidised with chromic mixture, it yields benzoic and acetic acids.

The formation may be expressed thus:—

$$\underset{\text{Benzoic aldehyde.}}{C_6H_5COH} + \underset{\substack{\text{Isobutyric}\\\text{anhydride.}}}{(C_4H_7O)_2O} = \underset{\substack{\text{Butenyl-}\\\text{benzene.}}}{C_6H_5.C_4H_7} + C_4H_8O_2 + CO_2.$$

Dibromide of β-Butenylbenzene.

On adding a standard solution of bromine in glacial acetic acid to a weighed quantity of this hydrocarbon, the colour of the bromine rapidly disappears, until about the theoretical quantity of bromine has been added to produce a dibromide. On adding water, a heavy oil separates. This, after being collected, washed with dilute alkali, and dried, appears as a colourless transparent and thick oil. It evidently has the formula $C_{10}H_{12}Br_2$.

This substance differs from the dibromide of *α*-butenylbenzene in being liquid; in fact, it cannot be made to solidify even when cooled to −20°, and well agitated with a glass rod, a few crystals of the *α*-dibromide being likewise added to it.

Bromo-β-Butenylbenzene.

The above dibromide when gently heated with an excess of alcoholic potassium hydrate, rapidly decomposes, potassium bromide separating in quantity. On adding water, a heavy oil separates. This is bromo-*β*-butenylbenzene, $C_{10}H_{11}Br$.

It is a transparent fluid more mobile than the dibromide.

Dibromide of Bromo-β-Butenylbenzene.

On dissolving bromo-*β*-butenylbenzene in a sufficient quantity of a ten per cent. solution of bromine in glacial acetic acid to form a dibromide, the liquid gradually becomes lighter in colour, and in the

course of an hour or two, begins to deposit crystals. After standing for about twelve hours, most of the bromine has disappeared, and the liquid is filled with crystals. These were collected, washed with glacial acetic acid, and then recrystallised from that solvent. In this manner the new body was obtained beautifully white, and like freshly sublimed benzoic acid.

The following numbers were obtained on analysis :—

·2205 of substance gave—

·2615 of CO_2, and
·0604 of H_2O.

The formula $C_{10}H_{11}Br.Br_2$ requires—

		Experiment.
Carbon	32·34	32·34
Hydrogen	2·96	3·04

This substance is therefore the dibromide of bromo-β-butenylbenzene. It melts at 63·5°, and when strongly heated decomposes, hydrobromic acid being evolved, and a colourless oily body distilling over. It is not very easily soluble in cold, but readily in boiling alcohol. Both ether and petroleum spirit dissolve it freely in the cold. It is not very easily soluble in boiling glacial acetic acid, and very slightly soluble in the cold acid.

When boiled with alcoholic potassium hydrate, it rapidly decomposes, with formation of potassium bromide and a heavy brominated oil. With an alcoholic solution of silver nitrate, it rapidly decomposes when heated, with formation of silver bromide.

Fuming nitric acid dissolves it, with formation of red fumes. On adding water to the product of the reaction, a thick yellow oil separates. Cold concentrated sulphuric acid does not dissolve it.

The formation of dibromide of bromo-β-butenylbenzene confirms the formula given for bromo-β-butenylbenzene.

Dibromide of α-butenylbenzene yields with alcoholic potassium hydrate, potassium bromide and an oily bromobutenylbenzene. This when treated with bromine yields only an oily derivative; all endeavours to obtain it in a crystalline condition have failed.*

* α-Butenylbenzene is somewhat difficult to obtain in quantity, the hydriodophenylangelic acid, when treated with alkaline solutions, being to a large extent reconverted into phenylangelic acid. As the dibromide of α-butenylbenzene had not been analysed, a portion was submitted to combustion, and gave the following numbers :—

·1097 of substance gave—

·1641 of CO_2, and
·0416 of H_2O.

The formula $C_{10}H_{12}Br_2$ requires—

		Experiment.
Carbon	41·09	40·79
Hydrogen.....	4·1	4·17

β-Isopropylbutenylbenzene.

On boiling a mixture of fifteen parts of isobutyric anhydride, ten of cuminic aldehyde, and five of sodium isobutyrate, large quantities of carbonic anhydride are produced, and the resulting product when distilled with water, yields a large quantity of an oil. This was washed with alkali, and then distilled with solid potassium hydrate, and finally several times with sodium; when fractioned, the principal part came over between 234° and 235°. On analysis, it gave the following numbers:—

I. ·1538 of substance gave—
·5037 of CO_2, and
·1430 of H_2O.

II. ·1549 of substance gave—
·5070 of CO_2, and
·1456 of H_2O.

The formula $C_{13}H_{18}$ requires—

		Experiment. I.	II.
Carbon	89·65	89·31	89·26
Hydrogen	10·35	10·33	10·44

This substance is therefore an isopropylbutenylbenzene: its formation may be expressed thus:—

$$C_6H_4(C_3H_7)COH + (C_4H_7O)_2O = C_6H_4\begin{cases} C_3H_7 \\ C_4H_7 \end{cases} + C_4H_8O_2 + CO_2$$

Cuminic aldehyde. Isobutyric anhydride. Isopropylbutenylbenzene.

This hydrocarbon differs from that I have previously described (*Jour. Chem. Soc.*, 1877, **2**, 665). Its boiling point is considerably lower—about 8°; and when treated with bromine-water, it forms a liquid dibromide instead of a solid one. I therefore have called it *β-isopropylbutenylbenzene*. Its specific gravity at 15° is 889.

Butenylcinnamene.

Ten grams of cinnamic aldehyde, fifteen grams of isobutyric anhydride, and seven and a-half grams of sodium isobutyrate were heated in a retort for about two hours. Carbonic anhydride was given off, and amounted to 2·5 grams. The product was mixed with water and distilled until no more oil came over with the water. The oil was separated and mixed with aqueous ammonia to remove isobutyric acid. It was then washed with water, collected and dried. When rectified, very little came over under 240°, but nearly all between

this and 260°. On distilling it with sodium, the principal fraction passed over between 248° and 250°. This was analysed, but the numbers were a little low. It was then left in contact with sodium for two days and frequently agitated. A certain amount of a brownish product formed. After this it was again distilled, and the portion boiling between 245° and 248° analysed. This last treatment with sodium apparently caused some of the hydrocarbon to polymerise, as the last portion had a very high boiling point.

The following numbers were obtained :—

I. ·1492 of substance gave—

·4957 of CO_2, and

·1222 of H_2O.

II. ·1610 of substance gave—

·5363 of CO_2, and

·1313 of H_2O.

The formula $C_{12}H_{14}$ requires—

		Experiment.	
		I.	II.
Carbon	91·13	90·61	90·84
Hydrogen	8·87	9·1	9·06

The formation of this hydrocarbon may be represented thus :—

$$\underset{\text{Cinnamic aldehyde.}}{C_6H_5.C_2H_2.COH} + (C_4H_7O)_2O = \underset{\text{Butenylcinnamene.}}{C_6H_5.C_2H_2.C_4H_7} + C_4H_8O_2 + CO_2.$$

Butenylcinnamene is a highly refracting liquid lighter than water. Its odour is somewhat pleasant and aromatic. It is very remarkable for the rapidity with which it oxidises. If a small quantity be left exposed to the air in a watch-glass for about twelve hours, it will become as thick as Canada balsam. With concentrated sulphuric acid it becomes orange-red in colour; heat is also given out, and a thick oily product forms, which is apparently a polymeride of the hydrocarbon. Fuming nitric acid acts upon it with explosive violence, boiling dilute nitric acid gradually changes it into a yellow oil. Chromic mixture rapidly oxidises it.

Butenylcinnamene combines with bromine. It also appears to form a compound with picric acid which crystallises in needles.

Ortho-butenylphenol.

On heating the sodium-derivatives of salicyl hydride with an excess of isobutyric anhydride, large quantities of carbonic anhydride were evolved, and a thick oily product obtained. This was first treated with water to remove sodium isobutyrate, and then boiled with alcoholic potassium hydrate to saponify the isobutyric derivative of the new substance which had been formed. Water was added and the

alcohol boiled off. On acidifying the alkaline solution, an oil separated which was collected and distilled. The first parts which came over contained isobutyric acid and salicyl hydride; all that boiled below 200° was rejected. The rest was shaken with cold aqueous potassium hydrate and then with ether to remove neutral products. The clear alkaline solution was heated and acidified with hydrochloric acid; and the oil which separated was washed with dilute ammonia to remove traces of isobutyric acid and salicyl hydride, and then distilled with water. It came over very slowly and sank as an oil in the receiver. After being collected and dried, it was distilled; a little came over between 220—223°, but most at 223—225°, and the residue principally between 225—230°, after which the temperature went up quickly. On cooling, the residue in the retort solidified, owing to the presence of propionic coumarin, formed from a small quantity of propionic anhydride in the isobutyric anhydride used.

A second experiment was made, using salicyl hydride instead of the sodium-derivatives.

Thirty grams of salicyl hydride, twenty-two grams of sodium isobutyrate, and forty-five grams of isobutyric anhydride were heated together for about four hours. The amount of carbonic anhydride evolved weighed 4·3 grams. The sodium isobutyrate was separated from the product by means of water, and the oil washed with dilute potassium hydrate, enough being used to make the liquid pretty strongly alkaline, but avoiding too large an excess. The undissolved oil, consisting mainly of the isobutyric derivatives of the new product, was separated, a little ether being used to facilitate this operation. The ether was boiled off and the oil saponified with alcoholic potassium hydrate; water was then added, the alcohol boiled off, and hydrochloric acid added in excess. The new product (which separated as a thick oil) was collected, washed with dilute ammonia, dried and distilled, all being collected that came over under 250° (a good deal of residue was left in the retort). The distillate was then fractioned and the portion coming over between 220—230° kept separate; this was again distilled, and the portions between 223—225° collected. This process is superior to the first one, but the yield of the pure new product is but small in either case.

It gave on analysis the following numbers:—

·1457 of substance gave—

·4310 of CO_2, and
·1064 of H_2O.

The formula $C_{10}H_{12}O$ requires—

		Experiment.
Carbon	81·08	80·67
Hydrogen	8·10	8·11

I propose to call this substance *orthobutenyl-phenol*. Its formation may be expressed thus—

$$\text{I.}\quad C_6H_4\left\{\begin{matrix}COH\\OH\end{matrix}\right. + \left.\begin{matrix}C_4H_7O\\C_4H_7O\end{matrix}\right\}O = C_6H_4\left\{\begin{matrix}COH\\O.C_4H_7O\end{matrix}\right. + C_4H_8O_2.$$

Salicyl hydride. Isobutyro-salicyl hydride.

$$\text{II.}\quad C_6H_4\left\{\begin{matrix}COH\\O.C_4H_7O\end{matrix}\right. + \left.\begin{matrix}C_4H_7O\\C_4H_7O\end{matrix}\right\}O = C_6H_4\left\{\begin{matrix}C_4H_7\\O.C_4H_7O\end{matrix}\right. +$$

Isobutyrate of orthobutenyl-phenol.

$$+ C_4H_8O_2 + CO_2.$$

$$\text{III.}\quad C_6H_4\left\{\begin{matrix}C_4H_7\\O.C_4H_7O\end{matrix}\right. + H_2O = C_6H_4\left\{\begin{matrix}C_4H_7\\OH\end{matrix}\right. + C_4H_8O_2.$$

Orthobutenyl-phenol.

It will be remembered that normal butyric acid and salicyl hydride, &c., yield butyric coumarin.

Orthobutenyl-phenol is a colourless oil boiling at about 223—225°, having a smoky and cedar-like odour; its sp. gr. at 150° is 1·0171. It dissolves in a solution of potassium hydrate, but requires an excess. Ammonia dissolves it only to a small extent.

With nitric acid it forms a yellow resinous product; chromic mixture acts on it with violence. It decolorises bromine-water quickly, yielding a thick oily substance. Picric acid dissolves in it with an orange-red colour. With concentrated sulphuric acid it forms a cerise-coloured solution; this, however, soon becomes turbid from the separation of a gummy product, soluble in boiling water.

A mixture of orthobutenyl-phenol and anisic aldehyde, treated with three or four times its volume of concentrated sulphuric acid, forms a rich purple fluid; on the addition of water a resinous product separates, most of the colour disappearing. This product dissolves in alcohol, with an orange-red colour, destroyed by ammonia. With salicyl hydride and sulphuric acid, this phenol likewise forms a purple solution, but rather redder than in the previous case. On addition of water, a dark-coloured product separates; this is slightly soluble in water with a red colour; it is also partially soluble in aqueous potassium hydrate, its colour becoming very weak, but on addition of acid it is again restored.

Orthobutenyl-phenol, when mixed with chloroform and an excess of strong aqueous potash, becomes slightly warm and pink in colour; this changes to purple when heat is applied, and a strong reaction sets in, the liquid boiling vigorously by itself. The colour then changes to greenish-red, and finally to orange. On adding water and boiling off the excess of chloroform which has been employed, a yellowish-red

solution is obtained and some resinous matter deposited. On filtering the solution and adding hydrochloric acid, an oil separates, which is probably butenyl-salicyl hydride. When distilled it is a nearly colourless oil. It does not appear to combine very freely with bisulphites.

Parabutenyl Phenol.

Paroxybenzoic aldehyde treated with isobutyric anhydride and sodium isobutyrate behaves in the same manner to salicylic aldehyde; the mixture gives off carbonic anhydride and a new phenol is obtained. The yield however is very small, a great deal of neutral products being formed. This phenol boils at about 230—235°; it is an oil, but when cooled in a freezing mixture, solidifies to a crystalline mass. I did not obtain it sufficiently pure for analysis, but there can be no doubt about its identity, as when heated with alcoholic potassium hydrate and methylic iodide it produces an oil having the characteristics of β-butenylanisoïl.

β-Para-Butenylanisoïl.

Twenty grams of anisic aldehyde, thirty grams of isobutyric anhydride, and fifteen grams of sodium isobutyrate were heated in a retort, the mixture boiled at about 180°, and carbonic anhydride came over in abundance during the first half hour. The heating was continued for three or four hours. The amount of carbonic anhydride evolved amounted to 3·9 grams.

The product was distilled with water and the oily part of the distillate collected and washed with ammonia; after being again separated it was dried over carbonate of potassium. On being cooled by a mixture of ice and hydrochloric acid, it solidified to a beautiful crystalline mass. This was very strongly pressed between calico in a powerful screw-press cooled below 0°. The solid product then obtained fused at about + 7°, and formed the chief part of the product. For further purification it was dissolved in about its own bulk of alcohol and again frozen, being well stirred at first. The solid mass was again pressed, and then appeared as a pure white waxy substance; this was powdered and exposed to the cold air* until any adhering alcohol had evaporated; it was then fused and distilled with sodium.

This substance gave on analysis the following numbers:—

·1284 of substance gave—

·3830 of CO_2, and
·1008 of H_2O.

* Of course these operations can only be conducted in winter time, when the temperature of the air is below 0°.

	Theory for $C_{11}H_{14}O$.	Experiment.
Carbon	81·48	81·35
Hydrogen	8·64	8·72

This substance I propose to call *β-para-butenylanisoïl*; its formation may be expressed thus:—

$$C_6H_4\begin{cases}COH\\OCH_3\end{cases} + \begin{matrix}C_4H_7O\\C_4H_7O\end{matrix}\Big\}O = C_6H_4\begin{cases}C_4H_7\\OCH_3\end{cases} + C_4H_8O_2 + CO_2.$$

Anisic aldehyde. β-Butenyl anisoïl.

In most of its properties this substance resembles the para-butenyl-anisoïl obtained from phenyl angelic acid (*Jour. Chem. Soc.*, 1877, **2**, 671). Its odour and taste are similar, and it is a solid crystalline body. Its fusing point, however, is only 8·5 or 9°, whereas the other is 17°. Its boiling point is 236—237°, or about six degrees lower than the above, so that there can be no doubt about its being isomeric. A number of preparations of this substance have been made, and in all these physical properties have been constant.

When oxidised with chromic mixture it yields anisic and acetic acids.

From the foregoing results we now know of two butenylbenzenes, two isopropyl butenylbenzenes, and two para-butenylanisoïls, obtained by somewhat analogous processes, one class being formed by the decomposition of the replaced angelic acid is prepared from the aromatic aldehydes by normal butyric acid, the other being produced from the aromatic aldehydes by the action of the isobutyric acid. The question to be considered is why are they isomeric?

We will consider the two butenylbenzenes. In the formation of the one I described some time since, it will be remembered that it was prepared from phenylangelic acid by abstraction of carbonic anhydride. First I would draw attention to the formation of this acid from benzoic aldehyde, and for simplicity sake we will assume that it is formed from this and butyric acid, instead of butyric anhydride.

$$C_6H_5.CH\underset{O\quad H}{\overset{\quad}{\quad}} + CH—CH_2—CH_2—COOH =$$

$$C_6H_5.CH{=}CH—CH_2—CH_2—COOH.$$

On separating CO_2 from this acid we get—

$$C_6H_5.CH{=}CH—CH_2—CH_2—\underset{\quad H}{COO} = C_6H_5.CH{=}CH—CH_2—CH_3 + CO_2.$$

Now if we take isobutyric acid what should we get?—

$$C_6H_5.CH\underset{O\quad H}{\overset{\quad}{\quad}} + CH(CH_3)—CH—COOH = C_6H_5.CH{=}CH—\underset{CH_3}{CH}.COOH + H_2O.$$

This acid, however, does not appear to be sufficiently stable to exist, and immediately splits up into carbonic anhydride and the hydrocarbon,

$$C_6H_5.CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH = C_6H_5CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}} + CO_2.$$

Now according to this equation, the hydrocarbons obtained by butyric or isobutyric acid ought to be identical.

Baeyer, on treating furfurol with isobutyric anhydride, obtained a furfurbutylene, and he evidently considered it to be formed in a manner analogous to the above, as he assumes that it is constituted thus—

$$C_4H_3O.CH{=}CH{-}CH_2{-}CH_3.$$

β-Butenylbenzene when oxidised yields benzoic and acetic acids, the formation of the latter showing that it probably contains CH_3. What can its constitution be? It is not

$$C_6H_5.CH_2{-}CH_2{-}CH{=}CH_2,$$

as Aronheim obtained this substance by acting on benzylic chloride and iodide of allyl with sodium, and found it to have a boiling point of 176—178° (*Deut. Chem. Ges. Ber.*, **5**, 1068).

It may be possible that the acid which is assumed to be formed when isobutyric anhydride acts upon benzoic aldehyde, on splitting up, does not give up the hydrogen of the COOH group to the carbon group with which it is in juxtaposition, but to one of the others thus—

$$C_6H_5CH{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH = C_6H_5.CH_2{-}CH{=}CH{-}CH_3 + CO_2.$$

This would appear not improbable, as there is only one other arrangement $-CH{=}C<^{CH_3}_{CH_3}$ for the group C_4H_7 than those in the three formulæ above given.

Of course any reasoning which is found to be true in the case of β-butenylbenzene, will be equally true in the case of all the other bodies described in this paper.

XX.—*On Aurin* (Part II).

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

In our first research on this subject (*Jour. Chem. Soc.*, 1873, 434), which we published some six years ago, we found that, on heating aurin with aqueous ammonia to 140—150°, a new colouring matter is formed, dyeing on silk and wool a redder shade than aurin, and occurring in commerce under the name of "red corallin" or "peonin."

A preliminary examination of this body showed that it contained nitrogen, but that it was a mixture and not a pure compound. As alcoholic ammonia acts more rapidly than an aqueous solution, we heated aurin with the former, and thus obtained a dark-red liquid, which dried up to an amorphous mass having a beetle-green lustre, and evolving aniline when heated with an alkali.

This observation induced us to continue the heating with ammonia. The colour of the liquid became gradually paler, and at last a yellowish solution was obtained, which is more quickly formed by heating the mixture to 180°. On the addition of water, a colourless, crystalline base is precipitated, which is also obtained in long glistening needles when aurin is heated with an excess of aqueous ammonia for 20 hours to 200°.

It dissolves in acetic acid with a splendid crimson colour, and gives with strong hydrochloric acid a dark-yellow solution, which on addition of water becomes red. These are the characteristic properties of rosaniline, and we had little doubt that this compound had been formed, as we could readily convert it, by well-known reactions, into Hofmann's violet, aniline-green, and aniline-blue. With these we dyed silk, wool, and cotton mordanted with antimony tannate, and obtained exactly the same shades as those given by rosaniline and its derivatives. Moreover, on comparing the spectrum of the hydrochloride with that of the rosaniline salt, we found them identical.

But there now arose a dilemma; if our formula of aurin, $C_{20}H_{14}O_3$, was correct, rosaniline could not be $C_{20}H_{19}N_3$; but Hofmann has proved it to have this composition by the analysis of its numerous derivatives, and therefore it appeared more probable that we had not found the true formula of aurin.

In order to decide these questions, we again prepared pure aurin according to the method already described. The pure phenol required for its preparation was again kindly presented to us by Messrs. C. Lowe and Co. It boils constantly at 181·5°, and not 184°, as we

formerly stated, the thermometer then used not being correct. The product was thoroughly boiled with water, dissolved in caustic soda, precipitated with hydrochloric acid, and after washing repeatedly crystallised from spirits of wine. The analyses of the compound thus obtained are given under 1 and 2.

Gräbe and Caro (*Liebig's Annalen*, **179**, 184), who also prepared aurin from pure phenol, say that by employing our process they succeeded in isolating from the crude product an aurin having the formula $C_{20}H_{14}O_3$, but much less easily than they expected after reading our paper, and that the principal products of the reaction consisted of bodies containing more oxygen, while Zulkowsky (*Liebig's Annalen*, **194**, 109) states that our method gave only wretched results, and could not be used for preparing aurin on a large scale.

The latter statement is quite correct, but the yield, although not very large, is far from being wretched, and the formation of bye-products can, if not entirely, yet to a great extent, be avoided by working under certain conditions, which, however, we are not allowed to publish, as our experience has been gained in works producing this colouring matter of an excellent quality.

This product we have also used to isolate aurin from, in order to procure quickly larger quantities, and at the same time to decide a question which we left open, *i.e.*, to ascertain whether the aurin obtained from the commercial product was identical or not with that prepared from pure phenol.

We find that they have exactly the same composition, but must at the same time state that the crude material used in our former experiments, and consisting of an amorphous, resinous mass, with a beetle-green lustre, was obtained from phenol containing some quantity of cresol, whilst that which we have since used was prepared from a much purer phenol; it consists of a red half-crystalline mass, having only a dull lustre. We isolated pure aurin from it by two methods.

The first we have already described. On passing ammonia into a saturated alcoholic solution of aurin, steel-blue crystals of ammonia and aurin soon begin to separate out. These were decomposed by dilute hydrochloric or acetic acid, and the product, after being well washed, was repeatedly crystallised from alcohol. The analyses of the product thus purified are given under 3 to 6.

The second method of purification was founded on the observation that the solubility of aurin in alcohol decreases with the removal of the bye-products contained in the commercial article. The latter was therefore washed with spirits of wine until only a comparatively small crystalline residue was left, which also was several times recrystallised from hot alcohol. Its analyses are given under 7 and 8.

A sign of the purity of aurin is, that it crystallises readily from alcohol in the form described by us.

The combustion of the different products gave the following results:—

	Aurin.	CO_2.	H_2O.
(1.)	0·2581	0·7427	0·1178
(2.)	0·3026	0·8708	0·1342
(3.)	0·2607	0·7515	0·1152
(4.)	0·2542	0·7317	0·1126
(5.)	0·2214	0·6397	0·0997
(6.)	0·3632	1·0457	0·1639
(7.)	0·3436	0·9878	0·1513
(8.)	0·3040	0·8766	0·1364

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)	(8.)
Carbon..	78·48	78·48	78·61	78·49	78·79	78·51	78·42	78·63
Hydrogen	5·06	4·92	4·91	4·92	5·00	5·07	4·89	4·99

From these numbers it follows that aurin consists of $C_{19}H_{14}O_3$:—

	Calculated.		Mean found.
C_{19}.....	228	78·62	78·55
H_{14}	14	4·83	4·96
O_3.....	48	16·55	16·49
	290	100·00	100·00

In order to confirm this formula, we prepared leucaurin by treating pure aurin with acetic acid and zinc-dust; it crystallised from hot dilute alcohol in large, flat, glistening needles, which, after being dried over sulphuric acid at 100°, were analysed with the following results:—

	Leucaurin.	CO_2.	H_2O.
(1.)	0·1896	0·5422	0·0970
(2.)	0·1601	0·4579	0·0828

	Calculated.		Found. (1.)	Found. (2.)
C_{19}	228	78·08	77·98	78·03
H_{16}	16	5·48	5·68	5·72
O_3	48	16·44	—	—
	292	100·00		

Whilst this research was progressing, the first news arrived of the results which E. and O. Fischer had obtained in their investigation of the different rosanilines.

By these researches our formula was confirmed, and it was shown

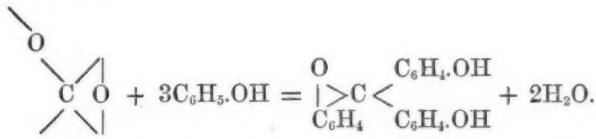
that the rosaniline which we obtained from aurin was para-rosaniline, $C_{19}H_{17}N_3$, or the lower homologue of common rosaniline. These chemists, as well as Gräbe and Caro, by their investigation of the different rosolic acids or aurins, have also established the constitution of these different compounds (E. and O. Fischer, *Deut. Chem. Ges. Ber.*, **11**, 195, 473, 612, 1079; Gräbe and Caro, *ibid.*, 1116, 1348).

The question which next arose was by what equation can the formation of aurin be explained. As the presence of free sulphuric acid probably produced complications in the reaction, we excluded it, and heated oxalic acid with pure phenolsulphonic acid. The reaction commenced only at 120°, and the products consisted of impure aurin, some formic acid, and free sulphuric acid. In order to avoid the action of the latter, barium phenolsulphonate was next employed, and thus the quantity of formic acid increased; the same result was obtained by heating sulphuric acid with a large excess of phenol, and gradually adding anhydrous oxalic acid. The quantity of gaseous products evolved during the reaction was but small, and they consisted of equal volumes of carbon monoxide and dioxide.

The formation of aurin can therefore be explained by the following equation:—

$$C_2H_2O_4 + 3C_6H_6O = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O.$$

In other words, oxalic acid is resolved into formic acid and the group O⩵C—O—, which by acting on three molecules of phenol produces aurin as follows:—



We have further examined several compounds and derivatives of aurin, and obtained some interesting results:—

Ammonia-aurin, $C_{19}H_{14}O_3(NH_3)_2$, is formed, as already mentioned, by saturating a concentrated solution of aurin with ammonia-gas. It crystallises in needles having a bright steel-blue lustre, loses ammonia very rapidly when exposed to the air, and crumbles into a reddish-brown powder of aurin. The compound used for analysis was dried in a current of ammonia, and an unweighed quantity put into a little flask with some water; the ammonia was expelled by boiling, collected in hydrochloric acid, and determined. The residual aurin was dried and weighed. As the following determinations show, the percentage of ammonia was found too high, which we expected, as the loose crystalline powder retained some of it mechanically; but the results leave no doubt that the compound has the above formula:—

	Weight of aurin.	Weight of $Pt(NH_4)_2Cl_6$.
(1.)	1·0970	1·8422
(2.)	0·9170	1·7554

	Calculated.		Found. (1.)	Found. (2.)
Ammonia	34	10·49	11·3	12·7
Aurin	290	89·51	—	—
	324	100·00		

The aurin which was recovered gave on combustion the following results :—

	Subst.	CO_2.	H_2O.
(1.)	0·2492	0·7176	0·1120
(2.)	0·2935	0·8473	0·1386

	(1.)	(2.)
C.....	78·53	78·73
H.....	4·99	5·24

Tetrabromaurin, $C_{19}H_{10}Br_4O_3$.—Gräbe and Caro (*loc. cit.*, 207) obtained tetrabromrosolic acid by gradually adding an excess of bromine to a solution of rosolic acid in hot glacial acetic acid. The compound separated in small, brownish-green plates having a metallic lustre; it was however not quite pure, but obtained so by recrystallisation from acetic acid.

On acting on aurin with bromine in the same way, a precipitate resembling tetrabromorosolic acid was obtained, which was washed with cold acetic acid and then heated with the same solvent, when the compound changed into a mass of small red needles, which on further addition of acid and continued heating, dissolved, and on cooling separated again as a magma. On concentrating the mother-liquor, steel-blue needles were obtained and the remainder of the liquid dried up to a smear. The determination of the bromine in the crystalline products gave numbers not in accordance with the above formula; the percentage of bromine varied and was much too high, showing that the original compound had undergone complete decomposition.

Pure tetrabromaurin is however easily obtained by adding a hot solution of aurin in acetic acid to a mixture of acetic acid and bromine containing an excess of the latter. The liquid remains clear for some time; then crystals begin to be formed, their quantity increasing on standing. When no more crystals separate, the mother-liquor contains hydrobromic acid and free bromine, but very little solid matter.

The small brownish-green crystals having a bronze lustre were

washed with cold acetic acid, dried at 100°, and the bromine determined with the following results:—

(1.) 0·2828 gave 0·3438 AgBr and 0·0049 Ag.
(2.) 0·2252 „ 0·2723 AgBr and 0·0052 Ag.

	Calculated for $C_{19}H_{10}Br_4O_3$.	Found. (1.)	(2.)
Br =	52·80 p. c.	53·01	53·15

Tetrabromaurin dissolves, like tetrabromorosolic acid, with a violet colour in alkalis, and dyes in an acidulated solution a deep violet on silk and wool.

Action of Acetyl Chloride and Acetic Anhydride on Aurin.—When we had found that by treating leucaurin with acetyl chloride, a triacetyl-compound is readily formed, we examined the action of the same agent on aurin. On heating them gently in presence of a little acetic acid, the aurin slowly dissolves with evolution of hydrochloric acid. From the pale yellow solution white crystals separated, which were recrystallised from alcohol and analysed. The results were not published, as we could not derive from them a probable formula; they are now given under 1 and 2.

We afterwards prepared this compound again, but, although we proceeded exactly as before, we did not succeed in obtaining it pure. In order to destroy an excess of acetyl chloride, the solution was precipitated with water, but the white crystalline powder soon became yellow, and then red on washing. On dissolving it in warm spirits of wine or acetic acid, yellow or reddish solutions were obtained, from which either steel-blue crystals or red needles having a blue metallic lustre separated out, or sometimes it dried up to a red amorphous mass, having a beetle-green reflection. Several of these products were analysed, but the results did not agree, and the percentage of carbon was always much too low for aurin, which might possibly have formed again.

After some trouble we found that the white compound is very easily decomposed when a small quantity of hydrochloric acid is present. We therefore heated the solution gently, when the reaction was finished, until all acetyl chloride was expelled. By adding water the white crystalline powder which was precipitated could without coloration be washed with water or crystallised from alcohol. Its analysis is found under (3).

As we had some difficulties in preparing this substance, we tried the action of acetic anhydride on aurin. On gently boiling, the latter soon dissolved to a yellowish liquid, which was mixed with alcohol to decompose the excess of acetic anhydride. Hot water was then added until a precipitate began to form; on cooling, small white plates crystallised out, having the same appearance as the compound ob-

tained from acetyl chloride, and identical with it, as shown by analysis 4, as well as with the compound which Gräbe and Caro prepared by acting on aurin with acetic anhydride in the cold or at 100°, and which is an additive product of the two bodies (*Deut. Chem. Ges. Ber.*, **11**, 1122).

This explains why it forms but slowly on heating aurin with a mixture of acetyl chloride and acetic acid, as the two latter must first, by elimination of hydrochloric acid, be converted into the anhydride, which then combines with the aurin.

Analysis gave the following results:—

	Subst.	CO_2.	H_2O.
(1.)	0·2062	0·5270	0·1060
(2.)	0·2630	0·6740	0·1275
(3.)	0·2529	0·6508	0·1242
(4.)	0·2658	0·6780	0·1240

	Calculated for $C_{19}H_{14}O_3 + C_4H_6O_3$.		(1.)	(2.)	(3.)	(4.)
C_{23}.....	276	70·41	69·69	69·88	70·18	69·57
H_{20}	20	5·10	5·70	5·38	5·40	5·18
O_6.....	96	24·49	—	—	—	—
	392	100·00				

According to Gräbe and Caro, this compound melts at 159—160°; we found the melting point higher, as all our preparations melted constantly at 168°.

The pure compound may be boiled with alcohol or acetic acid without undergoing any alteration; but on adding a small quantity of hydrochloric acid, the colourless solution rapidly turns yellow and then reddish-yellow; this change goes on very quickly in presence of acetic acid; on cooling, thin, slender, brown stellate needles crystallise out, which are obtained again in the same form by recrystallisation from hot dilute alcohol. This compound has not yet been examined more closely.

Combinations of Aurin with Acids.—Aurin possesses but feeble acid properties, and forms therefore with bases only unstable compounds. But on the other hand, it has the character of a strong base, combining with acids to form salts, which are very stable bodies and crystallise exceedingly well. The discovery of these remarkable bodies we have made by the following observations.

On heating aurin with a mixture of glacial acetic acid and acetyl chloride, the crystals lose at once their steel-blue lustre and assume a pale red colour. To obtain this compound in the pure state, acetyl chloride was added to a hot saturated solution of aurin in acetic acid. The liquid at once assumed a much lighter colour, and soon pale red

needle-shaped crystals having a diamond lustre separated out. On crystallising them from alcohol, we obtained brown, long slender needles, which on a second recrystallisation became steel-blue; a third did not alter their appearance, but a fourth changed them into red, glistening, oblong, six-sided plates, which by analysis were found to consist of pure aurin:—

0·2703 gave 0·5973 CO_2 and 0·0971 H_2O.

C ..... = 78·57
H ..... = 5·21

On treating the original crystals with water, they became dull and brownish-red, the solution containing free hydrochloric and acetic acids. It therefore seemed not improbable that the body was an additive product of aurin and acetyl chloride, containing, however, also acetic acid, for a superficial examination showed that the liquid contained, to one molecule of hydrochloric acid, much more than one molecule of acetic acid. We therefore next tried to get an analogous benzoyl-compound, and to determine in it, after decomposition with water, the relative quantities of hydrochloric and benzoic acids. On adding benzoyl chloride to a hot solution of aurin in acetic acid, similar crystals as before were obtained, which after being dried on filter paper in dry air, were treated with water, but only hydrochloric acid and acetic acid went into solution, and on heating the product with water or alkalis but a mere trace of benzoic acid could be detected.

These facts, coupled with a former observation that the bright-red needles, which, as we stated in our first paper, are formed by crystallising aurin from hot aqueous hydrochloric acid, retain the latter obstinately, led us to the conclusion that this acid forms a definite compound with aurin. Such a body could be formed under the above conditions, as our glacial acetic acid contained a little water. Moreover, Mr. Charles Lowe had informed us that the splendid specimen of aurin which he exhibited at Paris was obtained in the following way:—Pure phenol was heated with sulphuric acid, and oxalic acid gradually added. The crystalline product was dissolved in alcohol, and some strong hydrochloric acid mixed with it, by which a crystalline precipitate was formed, crystallising from hot acetic acid in beautiful, red, glistening flat needles. He was kind enough to give us a sample, and on examining it we found that water acted upon it in the same way as on our crystals.

To prepare a pure compound for analysis, a hot solution of aurin in acetic acid was saturated with hydrochloric acid gas; the colour of the liquid at once changed into a light yellowish-red, and soon the compound separated out in glistening needles, which, even when perfectly dry, smelt strongly of acetic acid.

When exposed to the air, they soon assume a steel-blue lustre, and gradually crumble into a brown-red crystalline powder. The same properties are shown by the crystals obtained from the acid chlorides and those prepared by Mr. Lowe. When heated to 110° in a current of dry air, they gradually lose all the acetic acid, which plays the part of water of crystallisation, and assume a dull-red colour.

On passing hydrochloric acid gas into an alcoholic solution of aurin, similar but smaller needles are formed, containing alcohol which is given off at 100°; the dull-red residue can, like the preceding one, be heated to 190° in a current of dry air, without losing hydrochloric acid, which only at 200° begins to escape.

In the first of these compounds, the acetic acid, aurin, and hydrochloric acid were determined as follows:—A weighed quantity was heated in a current of dry air until the weight became constant, and the residue washed on a weighed filter with cold water until the hydrochloric acid was washed out, which requires a long time, as traces of it obstinately adhere. Some aurin goes at the same time into solution, most of it in the beginning, as long as much free acid is present. The filtrate was precipitated with silver nitrate, and the aurin retained in the solution and the wash-water were determined by removing the excess of silver nitrate with hydrochloric acid, adding sodium carbonate to the filtrate until it became slightly alkaline, evaporating to dryness, exhausting with spirits of wine, evaporating again, decomposing the residual soda-compound with weak acetic acid, and washing the aurin thus set free with a small quantity of water.

The compound crystallised from an alcoholic solution was also dried at 100° in a current of dry air; the residue exhausted with boiling water, and only the hydrochloric acid contained in the solution determined.

The following analyses show that the dried compound consists of $C_{19}H_{14}O_3$, HCl:—

(1.) 0·6076 lost at 110° 0·1516 acetic acid, and gave 0·1776 AgCl, 0·0098 Ag, and 0·4064 aurin.

(2.) 0·6804 lost 0·1206 alcohol, and gave 0·2316 AgCl and 0·0076 Ag.

(3.) 0·7396 of the same compound, which had been pressed repeatedly between filter paper, lost 0·1226 alcohol.

	Calculated for $C_{19}H_{14}O_3$.HCl.		Found. (1.)	(2.)
Aurin.....	290·0	88·85	89·12	—
Hydrochloric acid..	36·4	11·15	10·60	11·05
	326·4	100·00	99·72	

The compound crystallised from acetic acid has, when dried at the ordinary temperature, the formula $C_{19}H_{14}O_3,HCl + 2C_2H_4O_2$:—

	Calculated.	Found. (1.)
Acetic acid	26·90 per cent.	25

That the numbers do not agree better is readily explained; the crystals easily lose acetic acid, and therefore smell strongly of it.

The crystals formed in an alcoholic solution seem to consist of $2C_{19}H_{14}O_3,HCl + 3C_2H_6O$.

	Calculated.	Found. (2.)	(3.)
Alcohol	17·8 per cent.	17·7	16·5

On adding a little sulphuric acid to a hot saturated solution of aurin in acetic acid, prismatic crystals or flat, very glistening red needles separate on cooling, while from an alcoholic solution small red needles are obtained. The former contain acetic acid and the latter alcohol, which they lose when heated in a current of dry air, a dull-red powder being left behind, which water resolves into aurin and sulphuric acid; traces of the latter stick, however, as in the case of the hydrochloride, obstinately to the aurin, even after prolonged washing with hot water.

The analysis of the dried compounds gave numbers which are not quite in accordance with those required by theory, but leave no doubt that the sulphate from alcohol has the composition $(C_{19}H_{14}O_3)_2SO_4H_2$, and that from acetic acid is the acid salt, $C_{19}H_{14}O_3,SO_4H_2$.

We have also prepared a nitrate, which is readily formed and crystallises well, but not analysed it yet.

Our endeavours to obtain an acetate were not crowned with success, although we expected to obtain such a compound very readily; for as we have stated in our former paper, we had observed that aurin retains acetic acid most obstinately. On crystallising the compound, which we had isolated from the commercial product from boiling glacial acetic acid, we obtained glistening red plates, which acquired a perfectly constant weight at 100°, and consisted, as analysis showed, of pure aurin. To this we must remark that only to the aurin, which we prepared from the former commercial article, acetic acid adheres so strongly. As we are still in possession of some of the latter and the preparations obtained from it, we intend to examine this subject again.

In our first paper we described a compound of sulphur dioxide and aurin. This is easily obtained in bright-red crystals by passing the gas in a hot alcoholic solution of aurin. We found our former observation, that the crystals are free from alcohol, but contain water, con-

firmed. This compound differs from the preceding salts, that it is not decomposed by water; no smell of sulphur dioxide could be perceived even on boiling, but on adding a drop of sulphuric acid, the gas was at once given off. We formerly stated that it could be heated without alteration to 100°, but we now find that such is the case only if it be exposed to that temperature only for a short time. On heating it in a current of dry air, it soon gives off water and sulphur dioxide. We therefore analysed a freshly-prepared sample of the air-dried compound, and obtained numbers closely agreeing with those formerly found, and leading to the formula $(C_{19}H_{14}O_3)_2SO_3H_2 + 4H_2O$.

0·7698 lost at 180° 0·1648 water and sulphur dioxide.

0·7918 gave 0·2573 $BaSO_4$.

	Calculated.	Found. Dried at 100°.	Found. Air-dried.
$C_{19}H_{14}O_3$.....	79·02	79·09	78·59
SO_2	8·72	8·50	8·92
H_2O	12·26	—	—

As we have previously shown, aurin forms very characteristic compounds with the acid sulphites of the alkali-metals, which, in accordance with the new formula, must now be written as follows. It will be seen that the experimental numbers agree much more closely with the calculated ones, than was formerly the case, and thus offer a fresh proof, if one were needed, that aurin has the formula which is now given to it.

	$C_{19}H_{14}O_3.SO_3KH$. Calculated.	Found.
K	9·51	9·14
S.....	7·80	7·45

	$C_{19}H_{14}O_3.SO_3NaH$. Calculated.	Found.
$C_{19}H_{14}O_3$.....	73·60	73·72
Na	5·84	6·12

	$C_{19}H_{14}O_3.SO_3(NH_4)H$. Calculated.	Found.
$C_{19}H_{14}O_3$.....	74·55	74·36
NH_3	4·38	4·23

The compounds of aurin with the acids have, like aurin itself, a red colour, whilst those with the acid sulphites and acetic anhydride are colourless like leucaurin. This seems to point out that the members of these two groups differ in constitution. We do not intend for the present to offer any speculation on this subject, but will only remark, that aurin contains an atom of oxygen which is combined with two carbon-atoms, just as in the oxides of the olefines, which, like aurin, combine readily with acids.

We have also found that rosolic acid, $C_{20}H_{16}O_3$, combines with acids and forms salts, which crystallise readily. We think, therefore, that as it is a base, like aurin, its name ought to be changed, and, as it has only been obtained from rosaniline, we propose to call it rosaurin.

In the beginning of this paper, we mentioned that we had intended to study peonin more fully; this research is going on. We hope to get hold of the intermediate compounds undoubtedly existing between aurin and rosaniline.

We have also made some more experiments with the blue colouring matters, which are formed by the action of aniline on aurin, and found that, as we expected, that the final product possesses all the properties of a triphenylrosaniline.

The analytical work required for this research was performed with great care and zeal by Mr. L. T. O'Shea, to whom our best thanks are due.

XXI.—*On Two New Methods for the Estimation of Minute Quantities of Carbon,* (1) *Gravimetric,* (2) *Nephelometric, and their Application to Water Analysis, &c.*

By A. Dupré, Ph.D., F.R.S., Lecturer on Chemistry at Westminster Hospital, and H. Wilson Hake, Ph.D., F.C.S.

I. *On a New Gravimetric Method for the Estimation of Minute Quantities of Carbon.*

Some time ago it was stated by one of us (*The Analyst*, July, 1877) that small quantities of carbon could be advantageously estimated by burning a known quantity of carbonaceous matter in a current of oxygen, absorbing the carbonic anhydride so formed in baryta-water, and converting the resulting baric carbonate into baric sulphate. A final product is thus obtained which weighs nearly twenty times (19·4 exactly) as much as the amount of carbon originally dealt with.

We have lately been engaged in conducting a series of experiments with the object of perfecting this process and of eliminating, as far as is practically possible, the error of experiment likely to arise from the introduction of extraneous carbonic acid. To obtain sufficiently small quantities of carbonaceous matter, an aqueous solution of sugar was made, containing about 0·2 gram of sugar in 100 grams of the solution, and, for the various experiments, quantities of this solution ranging from less than 1 c.c. and upwards were weighed in porcelain

boats as rapidly as possible. The boats were then placed in an air-bath at a temperature of 100°, and after evaporation to dryness of their contents put under the desiccator ready for use. Such weighed quantities of sugar solution represented quantities of carbon varying from 0·00034 to 0·0134 gram. A special description of the manner in which the combustion of these quantities was effected will be necessary for the clear understanding of the process. A combustion-tube, open at both ends and about 24 inches long, is drawn out and bent downwards at one end at an angle of 120°, so that it may be conveniently attached to a Pettenkofer absorption-tube, the other end being connected by means of a caoutchouc stopper and glass tubing, with an oxygen reservoir. This combustion-tube is filled half way from the bent end with granulated cupric oxide, which may conveniently be held in position by plugs of asbestos or by platinum wire gauze, or by a combination of both. The connection with the oxygen reservoir being then made, the greater part of the tube is heated to redness, with the ordinary precautions, and a stream of oxygen which is first conducted through a long tube containing caustic potash, is passed over the glowing oxide of copper until the issuing gas ceases after long bubbling to cause any turbidity in bright baryta-water. As soon as this point is reached, the portion of the combustion-tube preceding the layer of cupric oxide is allowed to cool somewhat, and the tube is now ready to be connected with the absorption-apparatus, the preparation and filling of which are important details, and will best here find mention.

After careful rinsing with distilled water, the clean absorption-tube (which is about 3 feet long) is clamped in front of the furnace in such a manner that its bulb end is somewhat higher than the end to be connected with the combustion-tube. Both ends must be provided with convenient stoppers, consisting of a short piece of caoutchouc tubing closed with a small piece of glass rod. The stoppers being removed, air, which is first caused to pass through a tube containing caustic potash, is pumped through the tube for about two minutes, and it is then at once filled with baryta-water as follows. The baryta-water (strength 1·5 per cent. BaO_2H_2) is kept in a sufficiently large stock-bottle, provided with a caoutchouc stopper, through which pass two bent glass tubes, the long one for syphoning, the short one, to which a potash-tube is attached, being connected with a small hand bellows. In filling the absorption-apparatus the longer syphon-tube is connected with it by means of flexible tubing, and the baryta-water is forced over by a gentle pressure of the hand-bellows, the bulb-end of the absorption-apparatus being provided with a potash-tube. As soon as the absorption-apparatus is half filled, the flow of baryta-water is arrested, its ends are immediately closed with its stoppers, and it is

now ready for use. By means of these extreme precautions, necessarily requiring some length of description, the tube is filled with perfectly clear and bright baryta-water with the greatest ease and in a few minutes.

All that now remains to be done is to connect the absorption-apparatus with the combustion-tube, and having introduced the substance to be burnt, to proceed with the combustion. The two tubes being connected then, and the stream of oxygen regulated to a minimum, the caoutchouc stopper in connection with the oxygen reservoir is for a moment removed, and the porcelain boat containing the known weight of carbonaceous matter is rapidly inserted in the tube and pushed by means of a long glass rod immediately in front of the layer of oxide of copper. The caoutchouc stopper is then immediately replaced, the stream of oxygen continued, and the combustion is gradually effected in the ordinary way.* As soon as the substance is burnt, the stream of oxygen is allowed to flow somewhat faster for two or three minutes. The whole operation occupies from fifteen to twenty minutes. It may be observed that since the bubbles of gas, consisting of a mixture of carbonic anhydride and oxygen, have to pass through about 12 inches of baryta-water, the absorption is very complete, more so than would be possible in any other form of apparatus.

One combustion being finished, the absorption-tube containing the precipitated carbonate of barium is carefully stoppered and set aside for the process of filtration, a process which, since it again involves special precautions, will also require special description. Before proceeding to this, however, it must be mentioned that as soon as one combustion is concluded another may be begun, and as many as one dozen consecutive combustions may be made with the same tube, provided only that the absorption-tubes are ready to hand, the quantities of substance weighed out, and that portion of the combustion-tube preceding the layer of oxide of copper allowed to cool somewhat between each combustion. Allowing, for example, an interval of five minutes between every two combustions, under perfect working conditions, twelve such combustions might be performed in the space of four hours and a half.

We now come to the process of filtration. A funnel and filter are arranged to stand over a beaker containing a layer of caustic potash solution at the bottom, the whole being covered by a bell-jar which itself stands in a layer of caustic potash solution. The mouth of the bell-jar, which is immediately over the funnel, is closed by a thick caoutchouc cap with two narrow openings, one of which is provided with a caustic potash tube (soda-lime apparently answers equally

* All connections should be made so that the ends of the glass tubes to be joined are brought as near together as possible.

well), the other, which is temporarily stoppered, contains a straight glass tube, placed immediately over the filter, so that after the whole arrangement has been left some time to itself in order that all enclosed air may be free from carbonic acid, direct connection may be made with the Pettenkofer tube by means of flexible tubing sufficiently long to admit of some slight freedom of action; filtration may thus be carried on without danger of carbonic acid being introduced, the additional precaution being taken of compelling all air which passes through the Pettenkofer tube during this process of filtration to first pass through a tube containing caustic potash attached to the tube itself. The washing of the precipitate in the tube and on the filter is effected almost entirely with boiling water which has been previously saturated with carbonate of barium (solubility 1 in 15,000), but finally with a small quantity of pure boiling distilled water. After complete washing the tube is disconnected, and the filter finally rinsed round, while still under the bell-jar, by means of the long tube already mentioned, and which when not clamped can be moved freely in all directions. The bell-jar is then removed, and the precipitate is rapidly washed together to the bottom of the filter if necessary. Care is taken to introduce the hot water into the tube by means of a beaker and funnel, so that no carbonic acid from the breath may affect the result. This process of filtration and washing being effected (and occupying some fifteen minutes' time), all further danger of introducing extraneous carbonic acid is at an end, and we proceed as follows. The Pettenkofer tube, which may contain minute particles of baric carbonate which the washing has not removed, is rinsed twice with small quantities of dilute pure hydrochloric acid (about 1 in 50), and finally with distilled water; the rinsings are poured on to the filter, on which the greater mass of baric carbonate is already collected, the filter is further washed with dilute hydrochloric acid if necessary, and finally with distilled water; and the whole of the solution of chloride of barium, so formed, carefully collected in a small beaker: the quantity of such solution need not exceed 50 c.c. This solution of chloride of barium has next to be evaporated, best in a platinum vessel, on the water-bath. It is next transferred, when greatly decreased in bulk, to a much smaller platinum dish (weighing about 5 grams), and finally evaporated to dryness after the addition of a few drops of pure sulphuric acid. The dish and its contents have then to be ignited, the residue moistened with a drop of nitric acid and re-dried, and the whole re-ignited and weighed to conclude the operation. The quantity of sulphate of barium so obtained divided by 19·4 indicates the amount of carbon estimated in the operation. The balance used in these operations was a small assay balance, by Oertling, on which one-tenth of a milligram is a comparatively large quantity.

We have not hitherto succeeded in removing a minute trace of iron and some as yet unaccountable organic impurity from the various solutions used, although great care has been exercised to obtain them as pure as possible. Notwithstanding all precautions, the final sulphate of barium always gives some slight indication of the presence of these impurities, and in consequence of this, as well as owing to the absorption of traces of carbonic anhydride, in three blank experiments, in which the filtration was carried out as above described, the usual quantity of baryta-water being taken, a residue was obtained which would theoretically result from the introduction of three-tenths of a milligram of carbon, the actual figures being (*a*) 0·000300, (*b*) 0·000293, (*c*) 0·000283. We found it necessary, therefore, in the following carbon estimations made by this method, to make a correction of 0·0003 for constant error. We have little doubt, however, that this error may, with reasonable anticipation, be looked upon as capable of reduction. Obviously each experimenter must determine his own personal blank error. We submit the following analyses:—

Sugar taken.	Carbon taken.	Carbon found.
0·03192	0·01344	0·01340
0·01841	0·00775	0·00748
0·01271	0·00535	0·00551
0·00926	0·00390	0·00398
0·00325	0·00137	0·00163
0·00188	0·00079	0·00085
0·00081	0·00034	0·00027

It will be evident from the foregoing results that this gravimetric method estimates with considerable and adequate accuracy what may truly be called minute quantities of carbon, such as are found to be present in say one litre of so-called "first-class" potable waters.

II. *On a New Nephelometric* Method for the Estimation of Minute Quantities of Carbon.*

This method is dependent on the varying degrees of turbidity caused by the action of varying quantities of carbonic anhydride in a standard solution (about 2 per cent.) of basic acetate of lead. The two following experiments demonstrate the delicacy of this reaction, and the precision with which it may be employed to indicate and estimate minute differences in already minute quantities of carbonic anhydride, and consequently in more minute quantities of carbon.

* From νεφελη, a cloud.

Experiment I.—Dry carbonic anhydride from an iron bottle was allowed to bubble slowly and uniformly through water. 100 bubbles were found to be equal to 1·2 c.c. of CO_2, so that each bubble represented 0·000024 gram (taking 1,000 c.c. = 2 grams). 5, 10, and 15 bubbles were respectively passed into equal quantities of a clear solution and the resulting variation in turbidity observed, the marked differences in which were unmistakeable. This somewhat rough experiment permitted us to differentiate between the following quantities of carbonic anhydride, and therefore between the amounts of carbon which they represent, thus:—

5 bubbles CO_2 = ·00012 gram CO_2 = ·000033 gram carbon.
10 bubbles CO_2 = ·00024 gram CO_2 = ·000065 gram carbon.
15 bubbles CO_2 = ·00036 gram CO_2 = ·000097 gram carbon.

Experiment II.—We next endeavoured to determine, as nearly as possible quantitatively, the varying amounts of carbonic anhydride (and therefore of carbon) corresponding to the variation in turbidity from a known standard by the aid of an apparatus which is essentially an enlarged form of Mills' well known colorimeter.* A turbid solution was prepared by passing 40 bubbles of CO_2 (each bubble = 0·000026 gram of CO_2 in this experiment) into 240 minims of a bright 2 per cent. solution of basic acetate of lead. The turbidity so produced was very marked and very constant, showing no tendency to settle for some time. Quantities of 60, 80, and 100 minims of this solution were respectively added to 50 c.c. of pure distilled water, which had been previously boiled, and the solutions so produced examined and compared in the colorimeter. The mean of several readings (in tenths of an inch), which varied but slightly, gave the proportional lengths of the discs from the surface of the liquids [which we will for convenience sake term *turbidity lengths*] 3 : 4 : 5 = 60 : 80 : 100.

We may tabulate these results as follows:—

60 minims turbid solution = ·000260 gram CO_2 = ·00007 C.
80 „ „ = ·000347 gram CO_2 = ·000094 C.
100 „ „ = ·000437 gram CO_2 = ·00012 C.

From the results of these two experiments, we felt justified in concluding that by comparing the turbidity produced in a given quantity of basic acetate of lead solution by the carbonic acid resulting from the combustion of a known small quantity of carbonaceous matter with the turbidity produced in an equal quantity of basic acetate of lead solution by the carbonic acid resulting from the combustion of a

* We are now endeavouring to devise an absorption-tube which will at the same time serve as the colorimeter. All transfer of the turbid lead solution will then be avoided.

fairly comparable but unknown quantity of carbonaceous matter, we should be enabled, not only to differentiate accurately between such small quantities of carbon, but also adequately to determine, by such comparison, the actual amount of the previously unknown quantity of carbon.

To demonstrate this by actual experiment, as conclusively as possible, was our next object, and to this end we determined quantitatively by this chromometric method the amounts of carbon present in the residue from 50 c.c. and 100 c.c. respectively of the water from the Westminster Hospital cistern, taking as standards of comparison two known and approximately similar quantities of carbon as represented by sugar. At the same time we determined, by the first described gravimetric method, the amount of carbon contained in the residue from 200 c.c. of the same water. The results and details of these experiments are given under heading III of this paper and are, it will be seen, eminently satisfactory.

Of the special application of these two methods to the examination of potable waters we now propose to speak. It will be obvious, however, that the methods are *par excellence* methods for the estimation of extremely small quantities of carbon, and many applications will doubtless suggest themselves to chemists to whom this special feature may present particular advantages; one or two applications which occur to us are given under heading IV.

It may be remarked that the second method supplements the first in delicacy, that is to say, quantities which are no longer determinable by means of the first method are easily determinable by the second. Judging from our present experience, we may say that method I is applicable to the determination of quantities of 1 milligram of carbon and upwards, while method II allows of the determination of considerably smaller quantities, as will have been seen. It may be possible in method I to substitute for the baryta-water basic acetate of lead or other metallic solution, with advantage, without in other respects essentially altering the described mode of procedure; we reserve this point therefore for future consideration.

III. *Special Application of the foregoing Methods to Water-analysis, with Suggested Use of a Metallic Collapsive Evaporating Dish.*

In applying these methods to the examination of potable waters, we were enabled to prove the efficacy of an idea which had occurred to us with regard to the dish in which the sample of water is to be evaporated. This is generally of glass, and it is plain that, in addition to the trouble of transferring the residue in such dishes to the combustion-tube, the difficulty of cleaning them so as to avoid error from

the possible introduction of a minute quantity of extraneous organic matter would be considerable, more especially when, as in the present case, the quantity of water taken for analysis might be as little as 50 c.c. If a dish could be made which would admit of ignition before use, and of such thin material that it could easily be crushed and introduced bodily with its solid contents into the combustion-tube, a great advantage would be secured. After trying several metallic foils we found that dishes of thin silver foil could be made free from pin-holes, and though sufficiently stout to admit of ignition at a red heat in the muffle, could be easily handled, and finally, after use for evaporation, crushed and inserted with their contents into the combustion-tube. We find also that copper foil makes an admirable evaporating dish of this kind, but we have not yet made use of one experimentally.

Three silver foil dishes, of a diameter of about 3 inches and capacity of 50 c.c., were made for us by Messrs. Johnson and Matthey, and with due precaution we evaporated in them 200 c.c., 100 c.c., and 50 c.c. respectively of water from the Westminster Hospital cistern to complete dryness, after addition to each of an excess of phosphoric acid. The dishes containing the residues were respectively crushed and inserted consecutively into the combustion-tube and separately burnt in the manner described on p. 161, chromate of lead being substituted for oxide of copper, and of course like it first ignited in a current of oxygen. The carbonic anhydride resulting from the combustion of the residues from the 100 c.c. and 50 c.c. of water respectively were absorbed in two quantities of basic acetate of lead solution in the manner described on p. 161, substituting basic lead acetate solution for baryta-water. Two porcelain boats, containing respectively ·00016 gram (boat I) and ·00026 gram (boat II) carbon, represented by a corresponding quantity of sugar, were inserted consecutively into the same combustion-tube, and the carbonic anhydride resulting from their combustion also absorbed in basic acetate of lead solution. Finally, the four turbid solutions of basic acetate of lead were compared in the colorimeter, the results being given below. The carbonic anhydride resulting from the combustion of the residue from the 200 c.c. of cistern water was absorbed in baryta-water, and the basic carbonate so formed transformed into basic sulphate exactly according to the method described under heading I.

The results of these two series of analyses may be thus stated:—

A. *Comparison of Turbid Lead Solutions—Nephelometric Method.* The four turbid lead solutions were each made up to 50 c.c. and compared as regards their relative *turbidity lengths* as follows:—

Turbidity length of boat I (·00016 C.) = 1·92 in.
" boat II (·00026 C.) = 1·10 in.

Turbidity length of boat I (·00016 C.) = 1·92 in.
„ residue from 50 c. c. = 2·38 in.

Turbidity length of boat II (·00026 C.) = 2·2 in.
„ residue from 100 c. c. = 1·81 in.

From these data we may calculate the amount of carbon contained respectively in the residue from 50 c.c. and 100 c.c. of the same water, taking the two known quantities of carbon as standards, and we may also calculate the quantity of carbon in one of the known quantities taking the other known quantity as the standard.

Thus, taking boat I (·00016 C.) as the standard:—

	Carbon taken.	Carbon found.
Boat II.....	0·00026	0·000279
Residue from 50 c. c. water	unknown	0·00013*

Or taking boat II (·00026 C.) as the standard:—

	Carbon taken.	Carbon found.
Boat I.....	0·00016	0·000149
Residue from 100 c. c. water	unknown	0·00031

B. *Determination of Carbon in Residue from 200 c.c. Cistern Water by Gravimetric Method.* Weight of final sulphate of barium = 0·0191 = 0·00068 carbon in 200 c.c. cistern water.

The three main results of these determinations may be summed up as follows:—

By Gravimetric Method.

	C in 100,000 parts.
Carbon in residue from 200 c.c. = 0·00068 gram.....	0·34

By Nephelometric Method.

Carbon in residue from 100 c.c. = 0·00031 gram.....	0·31
Carbon in residue from 50 c.c. = 0·00013 gram.....	0·26

* The precipitate produced in the lead solution by the combustion of the water residues had a very faint brownish tint, which, faint as it was, tended rather to cause a slight under-estimation of the carbon. We are at present unable to say what caused this coloration, but we are trying to discover, and, if possible, to prevent it; when the carbon estimations in water residues will then become even more accurate than those given.

IV. *Other Applications of the foregoing Methods.*

(a.) *The Estimation of Carbon in certain Metals.*

(b.) *The Estimation of Carbonic Acid and of Volatile and Suspended Organic Matter in Air.*

Some preliminary experiments in this direction have convinced us that the accurate estimation of these important factors is fully within the scope of these processes.

As regards the application of these methods to the estimation of carbonic acid in atmospheric air, it will be in the recollection of most Fellows of the Society that Dr. Angus Smith proposed some time ago a rough and ready method based upon the principle that an observer can fix and retain in his memory, with considerable accuracy, a certain degree of turbidity corresponding to a known quantity of suspended carbonate of baryta; by producing an equal degree of turbidity with a known quantity of air a measure of the carbonic acid was arrived at. Further, it must be mentioned that since the above paper was written, and after proceeding to apply method II to the estimation of the carbonic acid and organic matter, in air, we learnt that in the year 1857 Hugo v. Gilm, at the suggestion of F. Mohr, estimated the carbonic acid in atmospheric air by absorption of the same in baryta-water, conversion of the carbonate of barium into chloride, and volumetric estimation of the chlorine in this salt. From this brief recapitulation it will be seen that both Dr. Smith's method, and that of Hugo v. Gilm, for the estimation of carbonic acid in the air, are obviously different from the methods described in this paper, nor has it been proposed by either of these authors to apply their methods to the estimation of the other two factors. It is to be noted, also, that in these estimations Gilm uses very much larger quantities than would be necessary in applying our method—viz., 20 to 40 litres, and that he neglected what we have found to be absolutely necessary precautions in conducting the filtrations in an atmosphere free from carbonic acid.

XXII.—*On the Action of Chlorine upon Iodine.*

By J. B. Hannay, F.R.S.E., F.C.S., Assistant Lecturer on Chemistry, Owens College, Manchester.

In a paper published some years since (*Chem. Soc. Jour.*, 1873, 815), I pointed out that experiments which I had conducted threw great doubt on the existence of a compound of chlorine and iodine, which Kämmerer had described (*J. pr. Chem.*, **83**, 83), and to which he had attributed the formula ICl_4. At the time that he described this compound, iodine monochloride was supposed to be a liquid body at the ordinary temperature, and as Kämmerer knew nothing of its property of solidifying after some days, he says that when it did solidify it decomposed into free iodine and iodine tetrachloride. This body he describes as a black, shining, crystalline substance resembling iodine. Now if it were a solid body so exactly resembling iodine, and formed in such a manner that the whole mass of the two bodies must have been intimately intermixed, one is tempted to ask the question, how was the new compound separated from the free iodine in a state sufficiently pure for analysis? Having allowed iodine monochloride to solidify at least 20 times, and never having noticed the decomposition mentioned by Kämmerer, I determined to make an examination of the whole subject in order to settle finally whether or not such an anomalous body existed. I was urged all the more to make this examination, as lately in Germany the existence of Kämmerer's tetrachloride was taken for granted in certain theoretical discussions.

In the first place then we know, as I before pointed out, that any sample of monochloride or trichloride of iodine always contains minute quantities of the other chloride. This is strongly the case with the trichloride, the great difficulty in obtaining which pure has caused several authors to describe it erroneously. It is generally described as being of a red colour, but when quite pure it is really of a very bright yellow. It can only be obtained pure in thin films when sublimed in a current of pure dry chlorine, and on standing even for a short time, it loses chlorine and becomes red. That the red colour is really due to the presence of monochloride, is, I think, clearly shown by the following analytical numbers. The yellow samples were prepared by subliming the trichloride into a weighed tube in an atmosphere of chlorine, then driving out the chlorine by a puff of carbon dioxide, and at once closing and weighing the tube. The method of analysis was similar to that given in my former paper—

	Red.	Yellow.	Calculated for ICl_3.
Cl.....	43·84	45·58	45·61
I	56·07	54·50	54·39
	99·91	100·08	100·00

Each of the numbers given is the average of three careful analyses, which differed at most by 0·2 per cent. It will be seen that with all the care taken the bright yellow samples contained some of the monochloride. This seemed to throw further doubt on the possibility of the existence of a tetrachloride in presence of free iodine, as it is certain that even the trichloride cannot exist in its presence. To set the matter finally at rest, the following experiment was tried:—A piece of stout soda-glass tubing of small bore was bent into the form of an M, and to the first limb was sealed a strong wide tube containing chlorine mixture, with the sulphuric acid sealed in a thin bulb. Some iodine trichloride was placed in the middle bend, and the further end hermetically sealed. The acid bulb was broken and the middle limb placed in a mixture of ice and salt. After some hours, when a sufficient quantity of chlorine had liquefied, the trichloride was seen to be completely dissolved—a reddish-yellow liquid. To find whether any stable compound had been formed, the middle limb was removed from the freezing mixture, and the last limb immersed. When the chlorine had all distilled, the trichloride of iodine was left as a dark yellow crystalline crust. Although the appearance was quite sufficient for identification, the tube was opened, and an analysis made with the following result:—

		Calculated.
Cl	45·52	45·61
I	54·40	54·39
	99·92	100·00

Thus it will be seen that no stable compound above ICl_3 exists, and that even in this body is in itself very unstable. As there might however exist an unstable compound containing a higher proportion of chlorine, the following method was used for this investigation:—A small tube bent at an obtuse angle and closed at each end by a very well ground glass stop-cock, was sealed to a chlorine apparatus made to stand a strong pressure. A weighed quantity of iodine trichloride was then introduced into the tube, and the end stop-cock being closed communication was open only to the chlorine apparatus. The tube with trichloride was placed in a freezing mixture, and whenever its contents became liquid, the joint between the chlorine apparatus and the tube was melted, the stop-cock being previously closed, and the tube with liquid removed and weighed. It was then entirely cleaned out and

dried and weighed. Thus data were obtained for finding how much chlorine was required to form a liquid with the trichloride. Two other experiments were done, one with monochloride and one with pure iodine, the results of which are given below. Of course very many trials were made before good results were obtained, the great difficulty in obtaining perfectly tight stop-cocks being the principal. It is always difficult too to make large quantities of chlorine under pressure, without the mixture frothing over into the other vessel. The stoppered vessel held only half a cubic centimetre, so that the chlorine which remained in the space over the liquid was not taken into account. The following are the results :—

Iodine trichloride used	0·2335
Liquid formed	0·3005
Gain per cent.	28·69
Calculated for ICl_3.....	30·41
Iodine monochloride used.....	0·2040
Liquid formed.....	0·3675
Gain per cent.	80·14
Calculated for ICl_3.....	87·51
Iodine used.....	0·2100
Liquid formed.....	0·4995
Gain per cent.	137·86
Calculated for ICl_3.....	139·76

It will be seen from the above figures that when liquid chlorine is added to iodine till a reddish liquid is formed, the elements present are nearly in the proportion ICl_3. This compound can scarcely be said to have a chemical existence, because on removing the pressure or raising the temperature it gives off chlorine. I watched carefully for the formation of any lower compound, but there was no change of any sort till ICl_3 was reached. I think that it may now be concluded that the body ICl_4 has no existence, for the two reasons, 1st, that the reaction for its formation is impossible, as no high chloride of iodine can exist in presence of free iodine; and 2nd, that careful experiments by which chlorine is added to iodine in the most advantageous manner, for the formation of a high chloride, fail to yield any indication of such a body. The pentachloride, if such it may be called, from the monochloride, will be seen to be low in chlorine, but this was caused by leakage, for although four experiments were done this was the only one fit for analysis.

XXIII.—*Investigations into the Action of Substances in the Nascent and Occluded Conditions. Hydrogen (continued).*

By J. H. Gladstone, Pres. C.S., F.R.S., and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

From our recent study of the behaviour of nascent and occluded hydrogen (*Chem. Soc. Trans.*, 1878, 306) we arrived at the opinion that these hitherto supposed different states of the element are very closely related, if not identical—that, in fact, the activity of the so-called nascent hydrogen is only the consequence of its intimate association with the metals employed to bring about the liberation of the element.

To test this conclusion still further, we determined to examine the action of nascent and occluded hydrogen on other bodies. The two acids, nitric and sulphuric, presented themselves to our mind more especially, because the results, whether they strengthened our hypothesis or not, would certainly assist in the elucidation of the chemistry of the action of metals upon these compounds.

Nascent Hydrogen and Nitric Acid.

The usual way of preparing nascent hydrogen is by acting on a metal by means of an acid, and the first idea might be that the action of nitric acid on zinc or some other metal would itself furnish the body upon which we intended to experiment. But a moment's reflection will show that the nitric acid in attacking a metal can only generate hydrogen by becoming itself a nitrate, and thus introducing a third body into the reaction, while every chemist knows that the nitric acid itself is actually more or less deoxidised; and how far this is dependent on, or independent of, nascent hydrogen, it is impossible to say. There seemed, in fact, to be only one source of hydrogen which was unexceptionable, that from the electrolysis of the acid itself. This electrolytic hydrogen is pre-eminently in a nascent condition, and it does not matter for our purpose whether we suppose that is the HNO_3 or the accompanying H_2O that primarily suffers decomposition.

We are not without former experiments on this subject. Faraday (*Phil. Trans.*, 1834) taught that in the electrolysis of very strong nitric acid no free hydrogen appeared at the cathode, but nitrous acid, and apparently, after some time, nitric oxide; further, that when the strong acid was mixed with an equal or greater bulk of water, hydrogen alone appeared, varying in quantity with the strength of the

acid or voltaic current, but equivalent to the oxygen at the anode. Bourgoin (*J. Pharm.* [4], **13**, 266—270), who has more recently (1871) investigated this subject, finds, like Faraday, that the strongest acid gives no free hydrogen at the cathode, but that hydrogen alone appears there only when very dilute acid is employed. When acids of the strengths 5·2 and 14·6 per cent. respectively were used, hydrogen only was set free at the beginning of the action; nitrogen subsequently made its appearance, and also ammonia, but these substances are most probably not produced by the action of hydrogen on nitric acid, but are secondary or tertiary products of this action.

It would appear, then, that electrolytic or so-called nascent hydrogen reduces strong nitric acid, but only imperfectly, or not at all, when diluted with an equal bulk or more of water. But if the oxidation of the freed hydrogen in this action results from its being in the occluded condition, the reduction of the acid would depend upon the strength only in so far as this facilitated the de-occlusion of the hydrogenised electrode, and the stronger acid might be expected to do this the more readily. And it follows that with a given strength of acid, the amount of free gaseous hydrogen should bear some relation to the rate at which the electrolysis takes place: for were the gas freed from its nitric radicle more slowly, or not faster than it could pass into the occluded condition, none should bubble through the liquid; but were the rate of production of the element greater than that at which it is absorbed by the platinum electrode, some should escape, the quantity depending on the excess of the former over the latter action. This view offers a satisfactory explanation of the general results so far as they go, obtained by both Faraday and Bourgoin, and our own experiments on the electrolysis of the acid still further increase its probability.

The apparatus used by us was Hofmann's arrangement for illustrating the composition of water electrolytically. Each experiment went on until the same quantity (35 c.c.) of oxygen collected at the anode. The results, with other particulars, are given in the annexed table (p. 174).

It may be observed that no free hydrogen was liberated in any of the experiments with the 68 per cent. acid, nor in the first with the 1 : 1 acid; but in the second experiment with this strength, where the rate of decomposition was five times greater than in the first, some was set free; in the third, where the decomposition proceeded still more rapidly, more; and in the fourth, where again it was faster, still more gas escaped oxidation. The same general result is obtained with the weakest acid, but the proportion of free hydrogen for a given battery power is much greater. Our explanation is, that in all the experiments of the first series, as in the first of the second, the hydro-

Grove's cells employed.	Strength of nitric acid.	Time of experiment.	Negative pole.		
			Reduction in c.c. of oxygen.*	Free hydrogen.	H equal to NH_3 found.
1	1 / 68·2 p.c.	3 hours	31·5	Nil	Nil
2	"	55 mins.	28·4	"	"
4	"	22 "	28·8	"	"
8	"	10 "	29·4	"	"
1	1 : 1	3 hrs. 35 mins.	30·6	Nil	Nil
2	"	42 mins.	29	2 c.c.	"
4	"	19 "	24·2	9 "	"
8	"	8 "	16·8	22 "	Trace
2	1 : 2	61 mins.	17	30 c.c.	2 c.c.
4	"	18 "	0·5	65·7	Nil
8	"	8 "	0·3	68·7	"

gen was occluded at least as fast as produced—in fact, it is probable that at no moment in any of these trials was the platinum electrode fully charged with hydrogen: but that in the second experiment of the second series the gas was produced a little more rapidly than it was absorbed and oxidised; in the third experiment more, and in the fourth still more; whilst in the third series the same relation obtains, but the weaker acid being less readily deoxidated by occluded hydrogen, a greater quantity of the gas escaped through the liquid than in the corresponding trials with the stronger acid.

There is one very curious feature of this action to which we would now direct attention. In the second, third, and fourth experiments with the 1 : 1 acid, the evolution of hydrogen gas at the cathode ceased almost entirely and quite suddenly in three minutes, and in the first experiment with the 1 : 2 acid in 40 minutes. This evolution of hydrogen at the beginning only of the electrolysis of nitric acid was noticed by Bourgoin, and some long time previously by Schönbein. The first of these investigators made no attempt to account for the fact, while the latter attributed it to some *peculiar* condition into which the platinum electrode becomes thrown. We, on the contrary, have traced it to the presence of nitrous acid, which we find almost entirely prevents the escape of hydrogen with a battery power of 8 cells, when present in the proportion of 0·059 gram to 100 c.c. of the 1 : 1 acid.

The study of the action of the copper-zinc couple on aqueous nitre

* Determined by permanganate of potassium.

solution taught us that nitrite and nitrate of potassium suffer, when in admixture, simultaneous decomposition, and it would appear that the same obtains with their hydrogen analogues; and, moreover, that the mixture oxidises hydrogen more readily than does nitric acid alone.

Occluded Hydrogen and Nitric Acid.

Nothing is known, so far as we are aware, regarding the action of occluded hydrogen on nitric acid, but Dr. Armstrong (*Chem. Soc. J.*, 1877, **2**, 82) found hydrogen in the gaseous products of the action of nitric acid on a sample of nickel which Dr. Russell had prepared by reducing its oxide in a current of the gas, and inferred that it was hydrogen which had been occluded, and therefore escaped oxidation. He suggested this also as a means of investigating hydrogen-palladium.

The metal platinum, as is well known, is not attacked by nitric acid, and readily occludes hydrogen. For these reasons the gas was associated with this metal in order to study its action on nitric acid. A quantity of the metal was obtained in the most favourable form by precipitation with an alkaline formate. To ensure freedom from possible reducing matter, after being thoroughly washed and dried, it was boiled with strong nitric acid, again washed, and once more dried with as little contact with the air as possible. Nitric acid was not in the least acted upon by the metal thus prepared. The pure finely divided platinum was then charged with hydrogen by heating to 100° C. and cooling in that gas.

In a preliminary experiment, it was found that on dropping some pure nitric acid (68 per cent.) on to about 30 grams of the elements, a violent action was at once set up, the heat produced being sufficient to render the metal red hot, and to make us greatly fear an explosion, which convinced us that occluded hydrogen has, in this combination at least, a very decided action on nitric acid. A quantitative experiment was made by pouring very quickly 40 c.c. of the same colourless acid on 20 grams of the hydrogenised metal, when signs of reduction were almost at once noticeable by the yellow colour of the liquid and the escape of a small quantity of nitrous fumes. In 15 minutes the liquid reduced a quantity of potassium permanganate corresponding with 0·0372 of nitrous acid, and contained 0·0025 gram of ammonia. In another similar trial but with 1 : 1 acid, the reduction in 15 minutes corresponded with only 0·015 gram of nitrous acid, and 0·0016 gram of ammonia, showing still further the analogy between the action of electrolytic and occluded hydrogen on nitric acid.

But although the fact is thus satisfactorily established that hydrogen, when associated with a metal not acted upon by nitric acid, may be readily oxidised by it, such might not be the case were the gas

associated with a metal that is itself acted upon by the acid. Now, palladium both occludes hydrogen and is acted upon by nitric acid, especially when the latter contains nitrous acid, and therefore we thought an experiment with palladium-hydrogen and nitric acid might give results of some interest in settling this point. 2·5 grams of palladium were associated with about 120 c.c. of hydrogen, and some 18 c.c. of 1 : 1 acid quickly poured on. The metal slowly but completely dissolved without a trace of gas being set free, from which it would appear that whether the hydrogen be associated with a metal itself acted upon or not, it is still readily oxidised by nitric acid.

Nascent Hydrogen and Sulphuric Acid.

Again, the only source of nascent hydrogen available is that from the electrolysis of the acid. Faraday, who investigated this action also in 1834, found that oxygen separated at the anode, and sulphur and pure hydrogen at the cathode (*Phil. Trans.*, 1834).

On studying this subject in the Hofmann's apparatus mentioned above, with pure redistilled oil of vitriol containing 98·2 per cent. H_2SO_4, and variable battery power, results were obtained agreeing with Faraday's. We observed, moreover, that immediately the action was started with two or more cells, the sulphur formed a film over the negative electrode, which increased but only with comparative slowness during the continuance of the experiment. This is significant, and no doubt has a very considerable influence on the relative proportions of the two elements set free, and very probably accounts for the appearance of free hydrogen at all, at least where the smaller battery power was employed: for this film must necessarily retard the occlusion of the freed hydrogen, and, therefore, according to our view, compel the greater part of the gas to escape out of the liquid. Evidence of the correctness of this reasoning was given by very carefully noting the amounts of gas set free in the first minute or two of the action, starting first with a clean and afterwards a sulphur-covered plate. With the latter a greater quantity of hydrogen always escaped for an equal amount of gas collected at the anode.

An idea of the amount of gas which escapes with different battery power, may be gathered by glancing at the annexed table. In each case the electrolysis went on until 11·5 c.c. of gas (oxygen, but with some ozone) had collected at the anode :—

Battery power.	Time.	Hydrogen.
2	3·5 hours	18 c.c.
4	1 hour	23 „
8	23 mins.	26 „

It might be expected that hydrogen acting on sulphuric acid would set free sulphurous anhydride thus:—

$$H_2SO_4 + H_2 = 2H_2O + SO_2.$$

We could not, however, detect this substance in any of the experiments just detailed. But the reason of this, we thought, might be found in the quantity of the occluded gas being at any moment of the experiments sufficient to combine, apparently in one operation, with the three available atoms of oxygen in the acid molecule; and that if the gas were presented much more slowly, evidence of this very natural chemical change would be forthcoming. An experiment was therefore started with one cell. The amount of action was exceedingly small, only about one and a half c.c. of gas being collected at the anode in ten days. At the cathode not a trace of gas or sulphur appeared, but the liquid there was found to contain an appreciable amount of sulphurous anhydride.

It appears, then, that hydrogen, when associated with platinum, reduces oil of vitriol very readily, and that when the gaseous element is present in very small quantity, sulphurous anhydride is one of the products. The appearance of sulphur on the metallic electrode always results, very probably, from the complete deoxidation of this latter compound, which is much facilitated, no doubt, by the viscosity of the medium in which it is produced. Proof that occluded hydrogen does really bring about this reduction of sulphuric acid we now give.

Occluded Hydrogen and Sulphuric Acid.

Palladium Hydrogen.—The metal was obtained in a finely divided condition, and hydrogenised in the usual manner. On heating for one hour at 100° in a current of carbonic anhydride, as described below, 5 grams of the non-hydrogenised metal with 10 c.c. of the 98·2 per cent. acid, little or no sulphurous anhydride was evolved; but on pouring a few c.c. of the acid on a little of the metal charged with hydrogen, the odour of the sulphurous gas was immediately noticeable. The fact that sulphurous anhydride is abundantly evolved under these circumstances was completely established by quantitative trials, particulars of some of which we subjoin.

Experiment A. 10 c.c. of the acid were poured on 5 grams of the hydrogen-palladium. The sulphurous anhydride as produced was driven from the acid which absorbs it, by bubbling carbonic anhydride through the liquid. This was continued for 40 minutes at the ordinary temperature, and five minutes at about 100°. The amount of sulphurous gas which formed was found by iodine solution to be 0·592 gram.

Experiment B. Similar to A. The sulphurous anhydride was, however, estimated at intervals, when it was found that—

0·457 gram formed in the first 30 minutes, at the ordinary temperature.

0·152 gram formed in the next 30 minutes at 100°, and

0·001 gram formed in the next 30 minutes at 100°,

making a total in the hour and half of 0·61 gram.

Experiment C. Used 20 c.c. of the acid. In all other particulars the same as B. The amount of sulphurous anhydride formed was—

0·344 gram in the first 30 minutes, at the ordinary temperature,

0·261 gram in the next 30 minutes at 100°, and

0·016 gram in the next 30 minutes, at 100°,

making a total of 0·621 gram.

Oil of vitriol, then, not only very readily oxidises occluded hydrogen, but, it would appear, from the amounts of sulphurous anhydride produced in the several experiments being almost identical, that a definite proportion of the gas (some 72·4 per cent.) when associated with palladium, suffers this change.

Hydrogen-palladium has also a very slight reducing action on sulphuric acid mixed with an equal bulk of water.

Hydrogen Platinum.—Hydrogen associated with finely divided platinum prepared as already described, reduces oil of vitriol to sulphurous anhydride, but much less energetically than palladium-hydrogen.

Two views appear to be held with regard to the formation of the reduction-products in the action of metals on nitric acid and oil of vitriol: one that they result from the direct reducing action of the metallic elements; the other, that the reductions are effected by nascent hydrogen produced by the initial action of the metals on the respective acids. These views are alike, in so far that both are based upon analogical rather than on experimental evidence. The first derives support from the fact that certain non-metallic elements are oxidated by the bodies in question; and the second, from the general behaviour of metals with the class of compounds designated acids.

Reasoning on the lines of this research, we saw that direct proof of the truth of the second, and more probable view, might not be impossible to find. Now, in order to obtain the evidence of the liberation of hydrogen which this view requires, it appeared only necessary to bring about the initial action at such a rate, that the liberation of the gas should be faster than it could pass to the occluded condition. And to ensure the greatest probability of doing this, it further appeared necessary to employ, firstly, the metal of maximum available activity, and, secondly, a large volume of acid relatively to the metal, in order to minimise the influence of reduction-products. Magnesium was natu-

rally suggested. In each of our experiments a piece of this metal in thin sheet (1 × $\frac{5}{8}$-inch), weighing 0·4 gram, was placed in the centre of 350 c.c. of the nitric acid liquid.

Experiment I. Used 68 per cent. acid. The metal became coated at once with a whitish powder, and very slowly dissolved, with evolution of a minute quantity of gas, the liquid, as the action proceeded, acquiring a yellow colour. In 54 minutes the metal remaining undissolved suddenly decomposed the acid, with almost explosive violence. The total gas collected measured only 3 c.c. It was neither combustible nor explosive.

Experiment II. Used 1 : 1 acid. The metal did not tarnish, but entirely dissolved in 1—2 seconds, with evolution of gas, the first 3 c.c. of which burnt almost noiselessly; the second 3 c.c. detonated slightly; and the next 6 c.c. burnt still more explosively.

Experiment III. Used 1 : 2 acid. The general result was the same as in II. A little more gas was evolved, and the first 3 c.c. burnt somewhat less noiselessly than the corresponding portion in II. Further evidence of the production of hydrogen appeared unnecessary.

Among other results of this investigation, then, we may claim to have demonstrated the possibility of the replacement of hydrogen in nitric acid by a metal, a fact which very greatly supports, and removes from the region of conjecture, the view which regards the reduction-products already referred to, as formed by the direct action of hydrogen. We may also claim to have established still more fully the close likeness of character, and therefore of condition, between hydrogen usually denominated *nascent*, and hydrogen occluded by metals.

XXIV.—*On Colouring Matters derived from Diazo-compounds.*

By Otto N. Witt, Ph.D.

Chemists who take an interest in one of the youngest branches of applied chemistry, the manufacture of artificial colouring matters, will have remarked that this industry has made during the last three or four years more rapid progress than ever. New colours are being constantly brought out, and a number of them have come into general use, having, if not replaced, at least greatly limited the use of some of the old, costly artificial, and especially of the natural dyes. Although, four or five years ago, the number of artificial colours was very considerable, their range was not perfect. There was a great variety of

magenta, violet, and blue shades; but only one green colour was known until quite recently, and this was of a very fugitive nature. Yellow colours were not known at all, and the only orange, phosphine, was a bye-product of limited production, and consequently very high in price. The dyer was therefore obliged to use for all the mixtures into which yellow or orange colours entered, the natural colours, such as turmeric, anatto, and quercitron, which are both inconvenient in their use, and very fugitive.

The difficulty of selecting from the vast domain of organic compounds those which, being dyes, were likely to fill the existing gaps, induced me to work out a kind of theory of the relation between chemical constitution and the colouring power of aromatic substances, an abstract of which I read three years ago before this Society. In this paper I pointed out that there existed a series of compounds, the colour of which was in close relation to their chemical constitution. The first link of this series is azobenzene.

$$C_6H_5.N{=}N.C_6H_5.$$

It is, although of deep yellow colour, not applicable for dyeing, because it is devoid of salt-forming groups. From azobenzene, however, by the successive introduction of amido- or oxy-groups, either basic or acid compounds may be derived, possessing strong affinities to textile fibres, which increase with every new salt-forming group introduced into the molecule.

Of the vast number of possible dyes of this class, all of which are yellow or orange, only two at that time were known, amidoazobenzene,

$$C_6H_5.N{=}N.C_6H_4.NH_2,$$

and triamidoazobenzene,

$$\begin{matrix} C_6H_4.N{=}N.C_6H_3.NH_2 \\ .NH_2 \qquad\qquad .NH_2, \end{matrix}$$

the first of which was too fugitive, although of a very bright yellow colour, and the second of too dull and reddish a shade, although very fast. It was a natural consequence to assume that the intermediate, then unknown, diamidoazobenzene would combine the freshness and beauty of amidoazobenzene with the strong affinities of the triamido-compound. At the time when I read my paper, I had convinced myself that such was the case, and diamidoazobenzene had become, under the name of *chrysoïdine*, an article of commerce.

For its preparation I adopted a method, which divided the two stages of the formation of amidoazo-compounds into two distinct operations. It is generally admitted that, if nitrous acid be allowed to act

on an excess of amido-compounds, one molecule of diazo-compound is formed in the first instance—

$$C_6H_5NH_2 + HONO + HONO_2 = C_6H_5N{=}N.NO_3 + 2H_2O.$$

This diazo-compound acts on another molecule of the amido-compound, forming the amidoazo-compound—

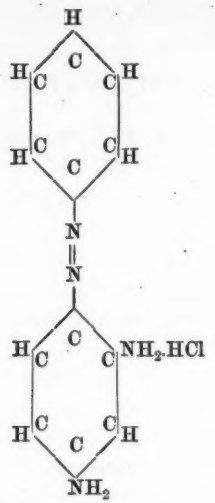
$$C_6H_5.NH_2 + C_6H_5.N{=}N.NO_3 = C_6H_5 - N{=}N - C_6H_4NH_2.HNO_3.$$

For the production of chrysoïdine I therefore prepared in the first instance a solution of diazobenzene chloride, which on being brought into contact with an aqueous metaphenylendiamine solution, deposited the hydrochlorate of chrysoïdine.

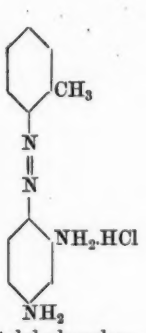
Griess has shown that not only amidoazo-compounds may be obtained, but that also the oxy-derivatives of azo-benzene and other azohydrocarbons—which are all dyes—may be prepared by acting with diazo-compounds on the corresponding phenols.

By introducing, therefore, the production of diazo-compounds in a pure state, and on a large scale, into the manufacture of aniline colours, an inexhaustible mine of new and beautiful dyes had been opened. When Hofmann published his paper on chrysoïdine, and explained the mode of its preparation, investigations on this class of colouring matters were instituted in the laboratories of almost all aniline colour manufacturers. At the present day the variety of azo-colours in the market, and the number of patents taken out for their production are constantly increasing. Several publications have appeared on the subject, some of which describe more or less accurately even the substances which I first prepared, and which are manufactured by Messrs. Williams, Thomas and Dower. I cannot therefore carry out my original intention of bringing before the Society a full description of the preparation and the properties of all my new azo-colours, and I must content myself with identifying those already described with the names which have been adopted for them in commerce, giving a full description only of some products, which hitherto have not been described by others.

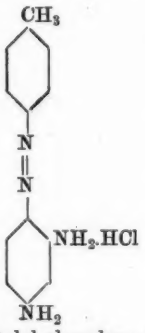
The prototype of these compounds is, of course, chrysoïdine, the hydrochloride of metadiamidoazobenzene—



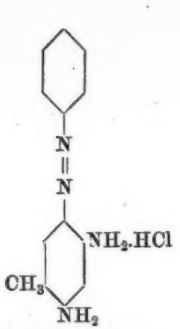
I have given a full description of its properties in a paper published in the *Deut. Chem. Ges. Ber.*, **10**, 654, and in abstract, in this Journal, 1877, **2**, 457, where I described its salts, the free base (m. p. 117·5°), its acetyl-derivative (m. p. 250·5°), and its sulpho-compound. I have since also prepared in a state of purity the following analogous substances, which in their properties differ but little from the typical product:—



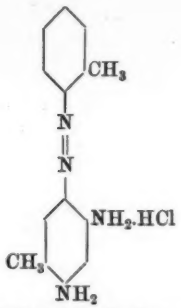
Orthotolyl-phenylene-chrysoïdine.



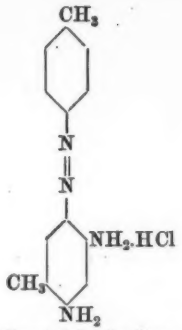
Paratolyl-phenylene-chrysoïdine.



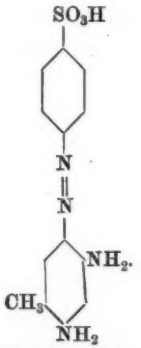
Phenyl-toluylene chrysoïdine.



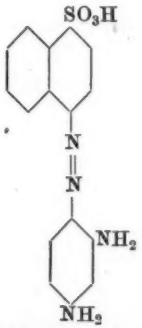
Orthotolyl-toluylene-chrysoïdine.



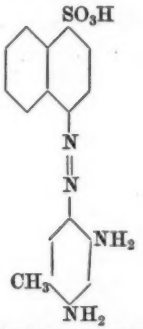
Paratolyl-toluylene chrysoïdine.



Phenyl-toluylene-chrysoïdine-sulphonic acid.



α-Naphthyl-phenylenechrysoïdine-sulphonic acid.

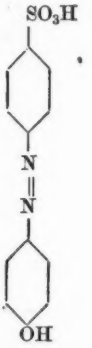


α-Naphthyl-toluylene-chrysoïdine-sulphonic acid.

I have already mentioned that to each basic colour belongs an acid one, which is similar in shade and constitution, and only containing hydroxyl in place of amido groups. Such is also the case with chrysoïdine, the acid counterpart of which has been prepared by Baeyer and Jæger (*Ber.* **8**, 51), and carefully studied by Mr. Typke (*Deut. Chem. Ges. Ber.* **10**, 1576). This compound is indeed a very beautiful dye, but its metallic salts have so little stability that it could not be employed in the usual way. I therefore introduced a sulpho-group into its molecule, originally by treating dioxyazobenzene with sulphuric acid at 100°; but very soon I adopted the action of paradiazobenzene-sulphonic acid on resorcin as a simpler method of preparation. This compound has since been described by Griess. Its constitutional formula is that of metadioxyazobenzene sulphonic acid—

and its acid sodium salt is sold under the name of *Tropæoline O*. By acting with diazobenzene sulphonic acid upon other phenols several other colouring matters have been obtained, of which I mention—

Tropæoline Y, the sodium-salt of monoxyazobenzene sulphonic acid, prepared from phenol.



Tropæoline OOO No. 1, oxy-α-naphthyl, and

Tropæoline OOO No. 2, or Orangé 2, the sodium-salt of oxy-β-naphthyl azophenyl sulphonic acid—

Trop. OOO No. 1.

Trop. OOO No. 2.

Tropæoline OOOO, which has been prepared by acting with diazobenzene chloride upon α-naphthol sulphonic acid. It is isomeric with tropæoline OOO No. 1, and OOO No. 2.

$$\alpha\text{-}C_{10}H_5 : SO_3Na$$

Another class of azo-colours may be obtained, if the salt-forming properties of amidoazobenzene and analogous compounds, the beautiful colour of which I mentioned already, be intensified by the introduction of one or several sulpho-groups. It is, however, more advantageous to start, not from amidoazobenzene itself, but from its methylated and phenylated derivatives. Thus we obtain, by acting with paradiazobenzene sulphonic acid on dimethylaniline, a compound which for some time has been manufactured by continental makers. The basic properties of the amidoazo-compounds are, however, still too prominent in it. The smallest quantity of acid introduced into its solution instantaneously reddens it. We may, however, obtain an appropriate equilibrium of basic and acid properties by introducing one phenyl- instead of two methyl-groups into the molecule of amidoazobenzene sulphonic acid, and thus produce perhaps the most beautiful azo-colouring matter known. This compound is manufactured and sold under the name of *Tropœoline OO*. Before describing its properties and derivatives I will make a few remarks on the corresponding non-sulphonated compound, *phenylamidoazobenzene*.

To prepare this compound I dissolve—

17 grams of diphenylamine in
100 c.c. of alcohol.

I also prepare by mixing the appropriate quantities of aniline, hydrochloric acid, and sodic nitrite a solution of

14 grams of diazobenzene chloride in
50 c.c. of alcohol.

I mix the two solutions, whereupon the mixture assumes a deep reddish-brown colour. The flask containing the mixture is surrounded by ice, and from time to time small quantities of an alcoholic trimethylamine solution are added to neutralise the hydrochloric acid liberated in the reaction. Trimethylamine is, on account of the solubility of its hydrochlorate in alcoholic liquids and its indifference to nitrous acid, a very useful reagent in such cases. In the present instance, however, care should be taken only to neutralise, not to basify, the mixture, which would be the case if sufficient trimethylamine were added to produce a yellow coloration. After some time, however, a point is reached when a single drop of trimethylamine solution produces this

yellow colour. The reaction is then finished. A quantity of a thick dark-brown oil has separated out, which may be increased by the addition of water. This oil, which solidifies after some time, is impure phenylamidoazobenzene. To obtain it in a pure state a somewhat lengthy purification is required. The crude product is dissolved in benzene, and the solution is precipitated with gaseous dry hydrochloric acid. The precipitate is collected, washed with benzene, and dried. It is then treated with aqueous ammonia solution, and the yellow mass obtained is carefully washed with cold water. It is then dissolved in alcohol, and for the quantity derived from one operation

50 c.c. of pure amylic nitrite and
25 c.c. of acetic acid are added.

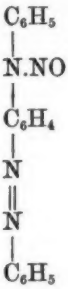
The mixture is heated on the water-bath until it begins to boil. On cooling a beautiful crystallisation of the nitroso-derivative is obtained. The crystals are collected, washed with alcohol, and boiled up with a mixture of equal volumes of alcohol and strong hydrochloric acid, when a reaction takes place. As soon as the formation of ethylic nitrite has ceased, the phenylamidoazobenzene is precipitated by the addition of water. It is collected, washed with ammoniacal water, and crystallised from a small quantity of alcohol, and finally from benzoline (petroleum, b. p. 90—148°), which removes the last traces of a black, tarry substance, tenaciously adhering to the impure product.

Phenylamidoazobenzene forms, when pure, leaflets or needles of a fine golden-yellow colour, m. p. 82°. It is soluble in benzoline, very soluble in alcohol, ether, and benzene. The alcoholic solution assumes a magnificent violet coloration on addition of hydrochloric acid, and after some time steel-grey needles of the hydrochlorate settle out. In concentrated sulphuric acid phenylamidoazobenzene dissolves with a green colour, which, on addition of water, changes into indigo, violet, and red. The analysis gave the following numbers:—

	Theory for $C_{18}H_{15}N_3$.	Found.
C.....	79·12	79·66
H	5·49	5·92
N.....	15·39	—
	100·00	

Its constitutional formula may be derived from its mode of formation, and the fact that it gives on reduction aniline and paramidodiphenylamine; it is therefore—

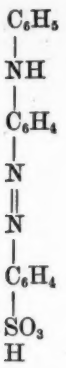
The description of amidodiphenylamine I must reserve for a paper on the reduction of the nitrodiphenylamines. Phenylamidoazobenzene forms, when treated with amylic nitrite and acetic acid as above described, a *nitrosamine* of the formula—



crystallising in beautiful orange needles, difficultly soluble in alcohol and acetic acid, very soluble in benzene, melting at 119·5°. Prolonged boiling with acetic acid causes a decomposition. Mineral acids regenerate phenylamidoazobenzene—

	Theory for $C_{18}H_{14}N_4O$.	Found. I.	Found. II.
C	71·60	71·54	71·96
H	4·60	5·39	5·37
N	18·50	—	—
O	5·30	—	—
	100·00		

If instead of acting with diazobenzene on diphenylamine, diazobenzene sulphonic acid be used, the product of the reaction is *Tropæoline OO*—



The free acid forms steel-grey needles, very sparingly soluble in water, with pink coloration. It is a powerful acid, and forms well-defined salts with most of the metallic oxides and organic bases, almost all of which are remarkable for their insolubility. The product in commerce is the *potassium salt*, slightly dichroic yellow and orange flat needles of considerable length and extreme fragility. It is very sparingly soluble in cold and easily soluble in boiling water. Very small quantities of mineral salts precipitate it from its solutions. The addition of mineral acids liberates the free acid and changes the colour of the liquid into a reddish-violet. This compound has therefore been proposed as an indicator in alcalimetry—.

	Theory for $C_{18}H_{14}N_3SO_3K$.	Found. I.	II.	III.
C	55·25	55·32	55·65	55·70
H	3·38	4·34	2·96	3·80
N	10·73	—	—	—
S	8·18	—	—	—
O	12·41	—	—	—
K	9·98	—	—	—
	100·00			

Sodium Salt.—Similar to the potassium salt, but not so well crystallised.

Ammonium Salt.—Very similar to the potassium salt.

Trimethylamine Salt.—The only salt of Tropæoline OO, which is easily soluble in cold water. It forms very beautiful flat needles.

Barium and calcium salts are insoluble yellow precipitates.

The *aniline salt* shows an extraordinary behaviour when treated with an excess of boiling aniline. It is then suddenly transformed into Induline, $C_{18}H_{15}N_3$, a blue colour, isomeric with phenylamidoazobenzene.

Tropæoline OO, yields on reduction sulphanilic acid and paramidodiphenylamine.

I trust I have succeeded in giving in the present paper a sketch of what I may be permitted to call genuine azo-colours, the true oxy- and amido-derivatives of azobenzene and analogous compounds.

The term *azo-colours* may, however, be extended to compounds derived from amidoazo bodies by the action of amines, and to other colouring substances containing the azo-group—

—N=N—

in their molecule. I hope to have an opportunity of bringing before the Society in another paper an account of my researches in this more intricate chapter of the chemistry of nitrogen.

XXV.—*On the Decomposition-products of Quinine and the Allied Alkaloïds.*

By J. J. Dobbie, M.A., B.Sc., Clark Scholar in Natural Science, University of Glasgow, and W. Ramsay, Ph.D., Tutorial Assistant of Chemistry, University of Glasgow.

Second Paper. Oxidation of Quinine, Quinidine (Conquinine), Cinchonine, and Cinchonidine, with Permanganate.

In our first paper on this subject we published the results of preliminary experiments on the oxidation of quinine. We have since continued those experiments, and extended our investigation to quinidine (conquinine), the isomeride of quinine, and to cinchonine and its isomeride, cinchonidine. All four bases yield on oxidation with potassium permanganate an acid, which, so far as our examination of its physical and chemical characters goes, is one and the same body. In the following paper, however, we have kept our results relating to the acid derived from each base separate, and, for convenience, shall refer to each acid by the name of the base from which it has been derived. The term "mixed acid" we shall use to denote acid obtained from residues containing oxidation products of all four alkaloïds.

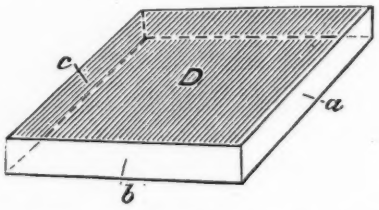
The oxidation was conducted in the manner already described; but the following method was found more convenient than that formerly employed for the separation of the acid.

The strongly alkaline liquor, filtered from the manganese oxide, was neutralised with nitric acid, and barium chloride added, which brought down the organic acid in the form of a curdy white precipitate. This precipitate, after thorough washing, was treated with sulphuric acid in quantity insufficient to decompose the whole

of the salt. The liquor containing the organic acid was filtered off and evaporated. The residue of barium salt remaining mixed with the sulphate of barium was afterwards treated with excess of sulphuric acid, filtered, and the organic acid in the filtrate precipitated as copper salt, and finally recovered by decomposing that salt with sulphuretted hydrogen. The acid prepared from the barium salt may be purified completely by a few crystallisations. The yield of acid from each base was over 10 per cent.

When pure, the acid crystallises in well formed, transparent, colourless plates, which usually grow together in clusters. For the following description of the cinchonine crystals we are indebted to the kindness of Mr. Baker, of the Owens College:—

"Rectangular plates, whose large faces are somewhat rough and generally curved, and whose edge-faces have an adamantine lustre. No other form was developed. Under the stauroscope no curves or crosses were seen, but the crystal depolarised the polarised light, appearing light on a dark ground.



First crystal.... $a : b$ 89° 58′ $b : c$ 89° 57′

179° 55′ instead of 180°.

Second crystal.. $a : b$ 90° 7′

Third crystal .. $a : b$ 89° 55′ $b : c$ 89° 45′

D : a 90° 7′.

So that all the interfacial angles are apparently right angles."

The crystals of the other acids are indistinguishable from those of the cinchonine acid.

When heated in a capillary tube in the paraffin bath, all four acids blacken at 200° C., and decompose at 256—257°. This behaviour has been confirmed by numerous experiments.

When dried at 100° for a considerable time, all four acids lose their water of crystallisation.

Cinchonine acid,	1·3597	gram	lost	0·1512	gram	= 11·1 per cent.
,, ,,	0·7346	,,	,,	0·0702	,,	= 9·55 ,,
Quinine acid ..	0·4360	,,	,,	0·0445	,,	= 10·2 ,,
Quinidine acid .	0·3020	,,	,,	0·0333	,,	= 11·0 ,,
,, ,,	0·0865	,,	,,	0·0992	,,	= 10·63 ,,

When the acid is acted upon with sulphuretted hydrogen, it is decomposed, with formation of a red amorphous substance, which is probably a reduction-product, and may be, as we before suggested, identical with Marchand's quinetin. When a mixture of the acid and this red substance is evaporated, at a certain point of concentration a violent action takes place, the red colour is discharged, and carbonic acid is evolved in quantity. It was on account of the decomposing action of sulphuretted hydrogen that the preparation of the acid from the lead salt was abandoned.

Combustion of the acid gave the following results:—

Quinine Acid.

Percentage of C and H.

·3463 gram acid gave ·5869 gram CO_2 ·0837 H_2O = 46·27 2·65
·2440 „ „ ·4143 „ „ ·0602 „ = 46·27 2·73

Cinchonine Acid.

Percentage of C and H.

·2595 gram acid gave ·4407 gram CO_2 ·0694 H_2O = 46·28 2·93

Quinidine Acid.

·3338 gram acid gave ·5697 gram CO_2 ·0780 H_2O = 46·52 2·56

Cinchonidine Acid.

·3330 gram acid gave ·5720 gram CO_2 ·0764 H_2O = 46·84 2·54

Mixed Acid.

·3551 gram acid gave ·6010 gram CO_2 ·0821 H_2O = 46·16 2·56

Nitrogen Determinations by Will and Varrentrapp's Process.

Quinine Acid.

Per cent. N.

·2733 gram acid gave ·1321 gram metallic Pt = ·01871 gram N = 6·84
·3189 „ „ ·1658 „ „ = ·02349 „ N = 7·36

Cinchonine Acid.

·3010 gram acid gave ·1555 gram metallic Pt = ·02203 gram N = 7·32

Quinidine Acid.

·3038 gram acid gave ·1547 gram metallic Pt = ·02192 gram N = 7·21

Cinchonidine Acid.

·3047 gram acid gave ·1658 gram metallic Pt = ·02349 gram N = 7·69

Mixed Acid.

·2931 gram acid gave ·1518 gram metallic Pt = ·0215 gram N = 7·33
·3017 „ „ ·1561 „ „ = ·0221 „ N = 7·36

Salts of the Acid.

The potash and soda salts of the acid, prepared by neutralising with potash and soda respectively, are deliquescent bodies very soluble in water, insoluble in alcohol.

Titration of acid with soda gave—

Cinchonine acid.....	24·84 per cent. Na.
Cinchonidine acid	24·70 „
Quinidine „	23·54 „

Titration of acid with potash gave—

Cinchonine acid.....	36·1 per cent. K.
Quinine acid (two experiments)	36·1 „

The ammonia salt was prepared by neutralising the acid with ammonia, and evaporating to dryness.

Mixed Acid.

0·4300 gram gained on evaporation 0·1200 gram = 21 per cent. ammonia.

Silver Salts.

Three silver salts exist. When the acid is neutralised with ammonia, and silver nitrate is added to the cold solution, a curdy white precipitate forms immediately.

Mixed Acid.

0·4445 gram of silver salt lost on ignition 0·1774 gram, leaving 0·2671 gram = 60·05 per cent. Ag.

0·4176 gram of silver salt lost on ignition 0·1690 gram, leaving 0·2486 gram = 59·54 per cent. Ag.

From boiling solution containing a little free nitric acid, after addition of $AgNO_3$, a salt containing less silver than the preceding, and crystallising in radiating tufts of long colourless needles, separated out.

Quinidine Acid.

·5787 gram salt gave ·3837 gram silver chloride = ·2888 gram Ag = 49·9 per cent. Ag.

·4670 gram salt gave ·2995 gram silver chloride = ·2262 gram Ag = 48·4 per cent. Ag.

·2790 gram salt gave ·1765 gram silver chloride = ·1327 gram Ag = 47·56 per cent. Ag.

·4100 gram salt gave ·3969 gram silver chloride = ·2997 gram Ag = 48·48 per cent. Ag.

·3252 gram salt gave ·2090 gram silver chloride = ·157 gram Ag = 48·5 per cent. Ag.

Quinine Acid.

·3283 gram salt gave ·2087 gram silver chloride = ·1576 gram Ag = 48·01. With regard to the first of the seanalyses, it may be well to note that there was no free nitric acid present in the solution. The silver salts decompose suddenly, even when heated up very gradually. On this account it is better to estimate the silver as chloride than as metallic silver after ignition.

The third silver salt, which crystallises in prisms of a faint yellow-green colour, was obtained from both the quinine and cinchonine acids, by adding to a hot solution containing free nitric acid, silver nitrate in quantity insufficient for the formation of the neutral salt. Our analyses of this salt were unsatisfactory, but sufficed to show that it contained much less silver than the preceding.

Calcium, barium, and strontium all form salts insoluble in cold water, and partially soluble in boiling water.

The *calcium salt*, prepared by adding calcium nitrate to a hot solution of the acid, separates out in beautiful satin-like flakes.

Mixed Acid.

·1341 gram salt gave ·0545 calcium carbonate = ·0218 calcium = 16·1 per cent. Ca.

The *barium salt*, prepared by adding barium chloride to hot solution of free acid, crystallises in oblong colourless plates. On analysis the salt from mixed acid gave 36·26 per cent. barium. A gelatinous salt, containing a higher percentage of barium, is formed when barium chloride is added to a solution of the acid neutralised with ammonia.

Mixed Acid.

·1461 gram salt gave ·1175 gram barium sulphate = ·06907 Ba = 47·26 per cent.

·3618 gram salt gave ·2895 gram barium sulphate = ·1682 Ba = 46·76 per cent.

The *strontium salt*, prepared in the same way as the calcium and barium salts, forms thick colourless plates or prisms pointed at both ends.

Quinidine Acid.

·3530 gram salt gave ·2050 gram strontium sulphate = ·09775 gram strontium = 27·69 per cent.

Mixed Acid.

·1905 gram salt gave ·1100 gram strontium sulphate = ·05239 gram strontium = 27·5 per cent.

Another experiment gave 28·07 per cent.

Lead Salt.—When lead nitrate is added to a hot solution of the

acid containing a little free nitric acid, the lead salt separates out on cooling in glistening white silky needles.

Cinchonine Acid.

Per cent. Pb.

·4365 gram salt gave ·3115 gram $PbSO_4$ = ·2128 gram Pb = 48·7

Quinine Acid.

·1250 gram salt gave ·0892 gram $PbSO_4$ = ·0609 gram Pb = 48·7

Quinidine Acid.

·4974 gram salt gave ·3530 gram $PbSO_4$ = ·2411 gram Pb = 48·67
·4863 „ „ ·3498 „ = ·2389 „ = 49·1

Zinc forms a beautiful salt, which separates in well-defined colourless crystals, having, when viewed through the microscope, the appearance of rhombohedra of Iceland spar.

Copper sulphate, added to the acid, gives a light blue heavy crystalline precipitate. We used this salt in working up the residues in preference to the lead salt. It is less apt to get into a slimy condition, and is more easily decomposed by sulphuretted hydrogen.

The *ethyl ether* of the acid is a crystalline body. It was prepared by passing hydrochloric acid gas into a solution of the acid in absolute alcohol. We have not yet analysed it.

In attempting to prepare the methyl ether by heating together the acid and methyl iodide, a tarry mass was obtained, which, on distillation, gave off pyridine freely.

An attempt to prepare the chloride by distilling the acid with phosphorous pentachloride gave a very decomposable crystalline substance, but in too small quantity for examination. The formula deducible from the analysis of the acid and its salts is $C_9H_5NO_6 + 1\frac{1}{2}H_2O$. Probably, from the fact mentioned in our first paper, that some of the salts on heating give off pyridine, the acid is tricarbopyridenic acid.

It is obvious from a comparison of the analyses of the salts that the acid is tribasic.

The potash, soda, ammonia, and silver salts, precipitated from neutral solution, are all normal salts, containing three atoms of metal. The following is a comparison of numbers found with those calculated from assigned formula for normal salts:—

Normal salt.	Calculated.	Found.
Soda	24·7	24·84 24·7 23·54
Potash	35·5	36·1
Ammonia	20·5	21·0
Silver	60·7	60·05 59·54

The gelatinous barium salt is also apparently a normal salt, in which three atoms of barium replace six atoms of hydrogen in two molecules of the acid.

The crystallised salts of barium, strontium, and calcium, as well as the crystallised silver salt, seem to be acid salts, containing one atom of dyad metal or two of monad metal, with one atom of replaceable hydrogen.

The third silver salt obtained by precipitation in hot acid solution probably belongs to the series of acid salts containing two atoms of replaceable hydrogen.

In the research by one of us on the dicarbopyridenic acids from picoline, it was found that the vapour-density of the decomposition-products of the acid, viz., pyridine and CO_2, corresponded with their decomposition according to the equation:—

$$C_5H_3N(COOH)_2 = C_5H_5N + 2CO_2.$$

We have made a similar experiment with the mixed acid, using the new form of apparatus described v. Meyer in the *Berichte* for 1879, No. 1. The vapour-density from the first determination gave 48·2, and that from a second determination 43·2. Supposing the acid to decompose according to the equation—

$$C_5H_2N(COOH)_3 = C_5H_5N + 3CO_2,$$

the vapour-density should be 26·3. On examining the contents of the bulb afterwards, it was noticed that charring had taken place, and that a crystalline substance had sublimed into the cool tube. This substance is not improbably an anhydride, formed by 2 molecules of the acid losing 3 molecules of water. A strong smell of pyridine was observed, showing that partial decomposition had taken place in the manner indicated by the equation.

The result of our investigation so far has been to confirm our hypothesis, that there is a close relation between the cinchona-bark alkaloïds and the bases of the pyridine series; and to prove that the four principal alkaloïds derived from the cinchona bark all yielded on oxidation one and the same acid.

We would draw attention to the fact that our first paper on this subject, in which we pointed out the close relation existing between the oxidation-products of quinine and those of the bases of the pyridine series, was published in March, 1878, in the *Journal of the Chemical Society*.

The *Berichte der Deutschen Chemischen Gesellschaft* for 11th February, 1879, contains an account (without analyses) by S. Hoogewerff and W. A. van Dorp, of the acid and some of the salts which we have described. We are glad to find that, as regards quinine, the results arrived at by those chemists confirm those which we had independently

obtained, and we hope that their investigation of the oxidation-products of the allied alkaloïds may also confirm those which we here publish. We are engaged in continuing our investigation of the acid, and of the other decomposition-products of quinine and the allied alkaloïds.

XXVI.—*On the Action of Isomorphous Salts in Exciting the Crystallisation of Supersaturated Solutions of each other, and some Experiments on Supersaturated Solutions of Mixed Salts.*

By John M. Thomson, King's College, London.

The history of the different views held by various investigators as to the causes producing or exciting sudden crystallisation of supersaturated solutions, has been so often and so well given on different occasions, that it is unnecessary to enter into a detailed description of these different opinions; suffice it to say that they may be placed under two headings, the first containing the idea that the crystallisation is induced by the entrance of a particle of the same salt; and the second, the supposition that a purely physical cause, such as the presence of greasy, fatty, or oily matter, in thin films, may be found active in exciting the crystallisation. The first explanation seems to be the most popular among the writers on the subject, among whom may be mentioned the names of Ziz, Gernez, and Violette, Dubrunfaut, Lecoq de Boisbaudran, and Liversidge. Of the latter view Mr. Tomlinson, in this country, is the chief supporter.

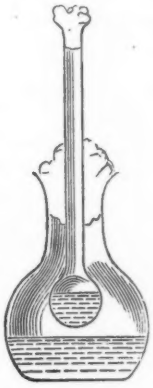
Some time ago I observed that a solution of potassium triiodide, prepared by Mr. Johnson, in the King's College Laboratory, remained under a desiccator for a considerable time without crystallising, but that shortly after the solution was exposed to the air, it was found filled with crystals of the triiodide. The solution had in fact undergone supersaturation, and as this particular body had not been prepared in the laboratory before, and as its deliquescent nature would most probably prevent its floating in the air as a solid, it obviously was not a particle of the salt itself which excited the crystallisation, and it appeared to me possible that a nucleus of some body isomorphous with the triiodide may have been the active agent in causing the crystallisation. I therefore determined to try the effect of a considerable number of substances, both isomorphous and also of different form and constitution on supersaturated solutions of each other, where it was possible to obtain such solutions. I may here mention that the

experiments detailed were repeated very many times, and that altogether over 400 observations were made.

Method of Experimenting.

One method employed in a large number of cases for the introduction of the nucleus into the supersaturated solution to be experimented upon, was as follows:—

1. *When the nucleus as well as the substance to be experimented on forms a supersaturated solution.*—The supersaturated solution to be examined was placed in a small flask, whilst a corresponding solution of the isomorphous salt to be employed as nucleus was placed in a very thin glass bulb, capable of being introduced through the neck of the small flask. The solution in the bulb-tube having been thoroughly boiled, the tube was stoppered with cotton wool, and then introduced through the centre of a second cotton wool plug into the neck of the flask. The contents of the flask were now again boiled, the contents of the bulb-tube receiving also a second boiling by the steam rising from the solution in the flask. The flasks so prepared were set aside to cool, and were generally not examined till after standing from 18 to 20 hours.

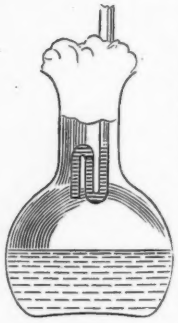


To perform an experiment, the solution of the body intended as nucleus contained in the bulb-tube was first crystallised by touching with a platinum wire, or, preferably, by introducing a crystal of the body contained in the bulb. Crystallisation having thus taken place in the bulb, and the crystal added having become covered by the deposit, the bulb was then lowered into the liquid contained in the flask, and allowed to remain there for some time, to show that the disturbance produced by the introduction of the bulb into the fluid did not cause crystallisation. The bulb was finally lightly broken in the fluid, and the result produced in the supersaturated solution observed.

It may be well to mention here that bulbs sometimes containing water, sometimes pieces of washed glass, were broken in the supersaturated solutions in a similar manner, to show that the disruption of the breaking of the bulb by itself produced no effect on the solution (the results in these cases being invariably negative). When the substance intended as a nucleus did not form a proper supersaturated solution, the same apparatus was employed, with this difference, that a hot saturated solution was placed in the bulb-tube, and having been thoroughly boiled, and the tube stoppered with cotton-wool, was allowed

to deposit crystals on cooling. As these crystals remained covered by mother-liquor, it may be inferred that nothing from the outside air could touch, and so vitiate the result.

2. The second method employed was that used by Prof. Liversidge (*Proc. Roy. Soc.*, xx, 497), in which, instead of a bulb-tube, a tube bent like a syphon, and drawn out slightly at the lowest end, was employed. Crystallisation was in this case induced in the first limb of the syphon tube, and allowed gradually to pass over the bend and down to the point of the second limb. As the expansion of liquids by rise in temperature is comparatively small, it was found to be quite easy, after a little practice, to fill the syphon tube with a hot, supersaturated solution of a salt isomorphous to that in the flask, wash it with warm water, place it in the neck of the flask, plug with cotton-wool both the tube and flask, and heat the whole apparatus to boiling, without the expansion of the liquid in the syphon tube causing any of the solution to drop into the lower flask. This method is not so applicable in those cases in which the nucleus does not form a supersaturated solution.



3. Experiments were also made with tubes or flasks covered with watch-glasses, or stoppered with cotton-wool, these being removed, and a thoroughly washed nucleus dropped into the solution, the plug of cotton or the watch-glass being again replaced. To render these experiments as free from error as possible, a tube or flask was always allowed to remain open and exposed to the air for a slightly longer time than the flask or tube experimented with, to show that during the experiment no nuclei floating in the air, and capable of causing crystallisation, had entered the flasks. The tubes containing the supersaturated solutions were also allowed to remain uncovered to the air for some seconds before the nuclei were added.

When crystallisation occurred in the test-flasks during the experiments, the results of these were discarded.

The substances employed in the solutions and as nuclei were in all cases carefully purified by recrystallisation, and other means, and were carefully tested before the experiments were performed. In those cases in which nuclei were added directly to the flasks from the air, they were in all cases carefully washed with ice-cold water before being dropped into the solution.

The following tables show the substances which were employed as supersaturated solutions, and also those added as nuclei.

Isomorphous Sulphates on Magnesium Sulphate.

Substance in solution.	Substance added.	Result.	Remarks.
$MgSO_4.7H_2O$	$ZnSO_4.7H_2O$	Active ...	Crystallisation induced at once, the crystals forming long needles.
„	$NiSO_4.7H_2O$	„ ...	
„	$CoSO_4.7H_2O$	„ ...	Crystallisation induced after some time, the crystals forming attached to the nucleus.
„	$FeSO_4.7H_2O$	„ ...	
„	$MgSO_4.7H_2O$	„ ...	
„	$NiSO_4.6H_2O$	„ ...	Crystallisation induced after some time, the crystals attached to the nucleus generally being truncated needles.
„	$FeSO_4.xH_2O$	„ ...	
„	$CoSO_4.xH_2O$	„ ...	

Dissimilar bodies on Magnesium Sulphate.

$MgSO_4.7H_2O$	$MgK_2(SO_4)_2.6H_2O$.	Inactive	
„	$Na_2SO_4.10H_2O$	„	
„	$Na_2S_2O_3.5H_2O$	„	
„	NaCl	„	
„	Glass	„	

Isomorphous Salts on Sodium Sulphate.

$Na_2SO_4.10H_2O$....	$Na_2SeO_4.10H_2O$ ...	Active ...	Crystallisation immediate.
„	$Na_2CrO_4.10H_2O$...	„ ...	„ „

Dissimilar bodies on Sodium Sulphate.

$Na_2SO_4.10H_2O$	$MgSO_4.7H_2O$	Inactive
„	Na_2SeO_4.....	„
„	$Na_2S_2O_3.5H_2O$	„
„	$Na_2HPO_4.10H_2O$ ..	„
„	KCl	„
„	NaCl	„
„	$KClO_3$	„
„	$NaI.4H_2O$	„
„	Glass	„

Chrome Alum and Iron Alum on common Alum.

$AlK(SO_4)_2.12H_2O$..	$CrK(SO_4)_2.12H_2O$	Active ...	The chrome alum solution was prepared by saturating at 70°, and then allowing it to crystallise in the bulb tube.
„ ..	$FeK(SO_4)_2.12H_2O$	„ ...	

Bodies of the same form or belonging to the same system, but not similarly constituted on Alum.

Substance in solution.	Substance added.	Result.	Remarks.
$AlK(SO_4)_2.12H_2O$ ..	NaCl (cubes).....	Inactive	
„ ..	FeS_2 (cubes).....	„	
„ ..	Fe_3O_4 (octahedra)..	„	

Hydro-disodic Phosphate and Hydro-disodic Arsenate.

$Na_2HPO_4.12H_2O$ ..	$Na_2HAsO_4.12H_2O$.	Active ...	Crystallisation immediate and very rapid.

Sodium Pyrophosphate on Sodium Dihydric Phosphate.

$Na_2HPO_4.12H_2O$ ..	$Na_4P_2O_7$.....	Inactive	

Sodium Acetate with Sodium Formate and Sodium Valerate.

$NaC_2H_3O_2.3H_2O$ ...	$NaCHO_2.H_2O$.....	Inactive	
„ ...	$NaC_5H_9O_2$.....	„	

The experiments above detailed were generally conducted according to the second method, the body employed as nucleus being added by means of the syphon-shaped tube; a large number of experiments was, however, conducted by the first and third methods; in this last case duplicate flasks of the supersaturated solutions being always exposed to the air during the experiment, so as to render the results as free from error as possible. The second method is, I think, upon the whole, the best, as with a little practice and care it can be employed for solutions of bodies which do not undergo supersaturation.

In those cases in which the sulphates $M''SO_4.7H_2O$ were used upon magnesium sulphates, the crystallisation in the cases of $NiSO_4.7H_2O$ and $ZnSO_4.7H_2O$, took place apparently at the same rate as if a crystal of the body itself had been employed, the crystals deposited resembling those of magnesium sulphates, which crystallise when the body itself is taken as the nucleus. In the cases, however, of $FeSO_4.7H_2O$ and $CoSO_4.7H_2O$, the crystallisation was apparently not so rapid, and the crystals deposited were often truncated needles formed and attached to the nucleus.

Some curious results were observed with the hexhydrated nickel

sulphate, $NiSO_4.6H_2O$, when employed as the exciting nucleus. In these cases immediate crystallisation did not take place, but after the nucleus had remained in contact with the solution for a short time, small crystals were observed attached to the nucleus, and spreading through the solution. These crystals were much more truncated than the crystals usually produced by a nucleus of $MgSO_4.7H_2O$, or of $NiSO_4.7H_2O$, and I am inclined to believe that they contain a different quantity of water. I have not as yet had time to prepare a sufficient quantity for analysis, nor to examine the other hexhydrated salts of the magnesium group of metals; some curious results, however, were found with crystals of the sulphates of cobalt and iron, containing quantities of water corresponding neither to the six-molecule nor the seven-molecule salts, these salts crystallising the magnesium solution after some time only. On analysis they were found to contain the following quantities of water:—

Substance.	Loss at 250° C.	Per cent. of H_2O.	Per cent. required for $CoSO_4.6H_2O$.	Per cent. required for $CoSO_4.7H_2O$.
·831. $CoSO_4.xH_2O$	·354	42·5	41·06	44·84
1·4. „	·606	43·2	„	„
			Per cent. required for $FeSO_4.6H_2O$.	Per cent. required for $FeSO_4.7H_2O$.
·521. $FeSO_4xH_2O$	·224	42·9	41·53	45·32
·862 „	·364	42·2	„	„

showing by these number that the amount of water in the crystals was too much for the six-molecule hydrate, but too little for the seven-molecule hydrate, and that probably the crystals in depositing from a warm solution may have contained a little of both, and that after some minutes' rest in the solution they broke up, the seven-molecule salt becoming active. The experiments with the sulphates of magnesium, nickel, and zinc, confirm some results published by M. Gernez, in 1866, in the *Ann. Sci. de l'Ecole Normale Supérieure*, but I have not been able to find that he has carried them any further in investigating any of the other isomorphous groups of substances in their action on each other.

The action of a double salt containing magnesium was also tried upon a supersaturated solution of magnesium sulphate, the one used being potassio-magnesic sulphate, $MgK_2(SO_4)_26H_2O$, which was found to be perfectly inactive to the magnesium solution. This result may be *considered* of interest as showing that probably some change in the relations of the substances has taken place with regard to their mole-

cular grouping, which now prevents the double salt from being active, although it contains the elements of magnesium sulphate.

A large number of experiments was also performed with bodies not isomorphous or similarly constituted to $MgSO_4.7H_2O$, and in all cases the nuclei remained inactive in the solution. Disturbance of the solution was also repeatedly made by the addition of pieces of glass which, when previously washed or heated, were invariably without action on the supersaturated solutions.

In the experiments upon supersaturated solutions of sodium sulphate, $Na_2SO_4.10H_2O$, the substances used were the selenate, $Na_2SeO_4.10H_2O$, and the chromate of sodium, $Na_2CrO_4.10H_2O$. The selenate was obtained as a specimen; and when tested by precipitating with barium chloride and boiling with hydrochloric acid no trace of sulphate was found.

The sodium chromate was prepared by neutralising carefully purified chromic acid with sodium carbonate, and allowing the crystals of the chromate to deposit by spontaneous evaporation. The chromate crystals showed no sulphate on testing. In the case of the selenate formed in the little bulbs or bent syphon-tubes, the sudden crystallisation of the solution contained in them invariably excited crystallisation of the sodium sulphate in the flasks. In a considerable number of instances, however, crystals of the selenate deposited in the tubes on standing were found to be without action on the sodium sulphate: they also possessed a slightly different form, being more truncated. The quantities of these crystals being very small, I have not as yet been able to determine the amount of water they contain, but I have little doubt that they will prove to be crystals of the anhydrous sodium selenate or of a hydrate containing less water than the ten-molecule salt which is the active substance.

With regard to the sodium chromate, I found it very difficult at first to obtain the crystals at all containing 10 molecules of water, as this salt effloresces very easily when removed from the mother-liquor. In preparing also the supersaturated solutions in the bulb or syphon-tubes, the sodium chromate is apt to deposit crystals of an inactive salt; but in all cases where the solutions of the chromate contained in these tubes were caused to deposit the salt by sudden crystallisation, the crystals so deposited were active to the sodium sulphate in the flasks. Experiments were also tried on solutions of sodium sulphate with bodies not analogous in form or constitution to $Na_2SO_4.10H_2O$, such bodies being found inactive to supersaturated solutions of that body.

In the case of common potash-alum, the other alums, chrome-alum and iron-potash-alum, were found to act as exciting nuclei with regard to it; but cubes of sodium chloride, also belonging to the regular system, were found to be without action on the alum solutions.

In order to see whether or not the form of the crystal alone had anything to do in rendering the substance capable of exciting the crystallising action, I determined to try the action upon common potash alum of substances possessing the same form but a different constitution, and for this purpose employed some octohedral crystals of magnetite.

These crystals were added to the alum solution, after being suspended in the neck of the flasks by means of horse-hair, and strongly cleaned by the steam from the supersaturated solution in the flask. When the solutions of alum had perfectly cooled, the crystals were lowered into the solutions and allowed to remain in contact with them for many hours, no sudden crystallisation being induced. A large number of experiments was also performed with cubes of copper pyrites on alum solutions in the same manner as those with magnetite without the induction of any crystallisation. Crystals of magnetite, thoroughly washed, could also be dropped into the alum solutions directly from the external air, without any crystallisation taking place, provided the surrounding atmosphere was thoroughly moist so as to dissolve floating nuclei; washed crystals, however, of chrome and iron alums at once induced crystallisation.

There are two other sets of experiments which have been performed, but in which, on account of the rarity of the reagents, I have not been able to obtain a sufficient number of results to justify a general conclusion upon them. The point examined in these experiments was the action of zinc selenate, $ZnSeO_4.7H_2O$, on magnesium sulphate, $MgSO_4.7H_2O$, and of $NaCl.2H_2O$ on a supersaturated solution of $NaI.2H_2O$; so far as they have gone, however, the experiments point to the result that crystals of these bodies are active to the solutions of similarly constituted substances. As will be seen in the table, however, the anhydrous chlorides and iodides of sodium, as well as potassium chloride, are inactive to the solution of sodium iodide containing two molecules of water: crystals of purified potassium chlorate are also inactive.

Thinking it might be of interest to examine the effect produced by change of constitution experienced in a series of organic acids, I examined the action of sodium formate, $NaCHO_2.H_2O$, and sodium valerate, $NaC_5H_9O_2.H_2O$, on a supersaturated solution of sodium acetate, $NaC_2H_3O_2.3H_2O$; neither of these substances crystallised to the solution of the acetate. I hope shortly to examine the effect of isomeric bodies in organic substances, as some interesting results may be looked for in these cases.

Experiments with Mixtures of ($MgSO_4.7H_2O$ + $Na_2SO_4.10H_2O$), ($MgSO_4.7H_2O$ + $NiSO_4.7H_2O$), *and* ($NiSO_4.7H_2O$ + $Na_2SO_4.10H_2O$).

Having found that a similarly constituted and perfectly isomorphous body caused the crystallisation of those substances which I had examined, I determined to try the action of nuclei on supersaturated solutions of mixtures. The solutions which I first employed were prepared by dissolving equal weights of the two salts separately in half their weight of water, and then mixing together equal volumes of the solutions so prepared. On adding a nucleus, consisting of one of the bodies employed, I found that although these solutions in the separate condition were thoroughly supersaturated when mixed, the addition of the individual nucleus did not cause any sudden crystallisation. The nucleus, however, on standing did not in these cases dissolve, but remained slowly growing in the solution. I performed a number of experiments with mixtures of ($MgSO_4.7H_2O$ + $Na_2SO_4.10H_2O$) prepared as stated above, using nuclei in these cases of $Na_2SO_4.10H_2O$; on decanting the supersaturated solution after the nuclei had remained in the solutions for several days, and had increased considerably in size, then dissolving and examining these nuclei, they were found to contain only sodium sulphate, and showed no presence of magnesium.

On finding that such solutions did not yield sudden crystallisation on the addition of one of the constituents, I prepared mixtures of the same salts in equal quantities, the total amount of the mixture being dissolved in half its weight of water, thus making each constituent dissolved, as it were, in a quarter the weight of water.

A number of flasks were prepared by dissolving 100 grams $MgSO_4.7H_2O$, and 100 grams $Na_2SO_4.10H_2O$ in 100 grams water and nuclei of the two salts taken separately were, after washing with ice-cold water, gently placed in the flasks, and the plugs of cotton wool replaced. It was observed that two distinct results may occur.

(A.) The nucleus may remain quietly growing in the solution without causing sudden crystallisation spreading through the mass.

(B.) The nucleus may cause sudden crystallisation, spreading through the solution gradually.

After allowing the nuclei in case (A) to remain for some days in the tightly plugged flasks, the mother-liquor above them was carefully decanted, and the crystals which had formed were quickly swilled with ice-cold water, pressed between blotting-paper, and quantitatively analysed.

The resulting crystals in the cases where $MgSO_4.7H_2O$ had been taken as the nucleus, were found to contain magnesium sulphate only. In testing these crystals, the magnesium was removed with baryta-

water, the excess of baryta by ammonium carbonate, and the residue evaporated with hydrochloric acid, when a sodium chloride was left.

The crystals from the $Na_2SO_4.10H_2O$ numbers were found to contain no magnesium sulphate, except in some of the flasks, when a mere cloudiness was seen on testing: the crystals in these cases were dissolved and tested with sodium phosphate and ammonia.

With the same solutions, when the result (B) took place, both substances were found in the crystals; and on quantitative determinations being made it was found that there was in every case a preponderance of the body of the same nature as the nucleus, the other substance being in such small quantities that it was evidently only carried down mechanically by the other salt.

In the case of isomorphous bodies the salts employed were mixtures of equivalent quantities of $MgSO_4.7H_2O$ and $NiSO_4.7H_2O$, the total quantity of the mixture dissolved in half its weight of water. In the case (B) of rapid crystallisation in these cases, both the substances were found in the crystals formed, and on making a quantitative determination they were found to exist in the same proportions as in the mother-liquor from which they were deposited. In some of the flasks containing the mixture of the isomorphous salts rapid crystallisation did not take place, but the nuclei remained undissolved and gradually increased in size. In these instances on making an analysis of the resulting crystals, it was found that, in the case of the magnesium and nickel sulphates at least, the nucleus had increased by a deposition of nickel sulphate only independently of whether the body added was $NiSO_4.7H_2O$ or $MgSO_4.7H_2O$. In fact, that in the slow crystallisation of a supersaturated mixture of these salts, which gradually approaches to ordinary crystallisation, the least soluble salt is the one which deposits. I hope shortly to be able to examine mixtures of other isomorphous salts if possible of the same, or nearly same solubility, to trace out further these relations, evidently relating to and depending on the different solubilities of the salt.

I have also examined a mixture of $NiSO_4.7H_2O$ and $Na_2SO_4.10H_2O$ in the proportions of $2(NiSO_4.7H_2O)$ to 1 of $(Na_2SO_4.10H_2O)$. In these experiments I have induced the crystallisation with $Na_2SO_4.10H_2O$ only, and have not as yet tried $NiSO_4.7H_2O$, and have observed that on touching the surface of the solution in the flasks very carefully with a minute crystal of $Na_2SO_4.10H_2O$, crystallisation commences from that point, and delicate plates shoot through the solution in different radiating directions, and appearing to travel along definite planes. On examining these they were found to consist entirely of sodium sulphate with only very small quantities of nickel sulphate attached, which could be easily removed by decanting the remaining mother-liquor and swilling with cold water.

I intend as soon as possible to continue the investigation of the action of nuclei on mixtures of similar and dissimilar salts, and to examine also the action of one or other constitutent when employed as a nucleus, on a supersaturated solution of a compound salt. I have, however, found considerable difficultly in preparing supersaturated solutions of true double salts, as most of them do not seem to yield such solutions easily. Some experiments have, however, been made with common potash alum in its behaviour to potassium sulphate; but before communicating these results, I wish to examine some other double salts, as very interesting results may be looked for from inquiries carried out in this direction, with regard to the conditions under which the constitnents of these salts exist when in solution. The following points may, I think, be taken as the general results to be deduced from the foregoing experiments.

The experiments of M. Gernez (*Ann. Sci. de l'Ecole Normale Supérieure*, 1866) have been extended and confirmed, showing that truly isomorphous bodies act as exciting nuclei in inducing the crystallisation of supersaturated solutions.

That mere form alone does not render the body active to a supersaturated solution of a salt isomorphous with the nucleus; but that it is necessary for the nucleus to possess an identical chemical structure, as is shown in the experiments with octohedral crystals of magnetite, and cubes of iron pyrites upon alum solutions.

In the case of the mixtures so far examined, that two series of results may be experienced with the same solution.

A. When the mixture consists of two salts which are not isomorphous.

(1.) Sudden crystallisation may take place, gradually spreading through the sclution on the addition of a nucleus, causing a deposition of the body belonging to the nucleus only.

(2.) That when sudden crystallisation takes place, causing the deposition of both salts, there is a preponderance of the salt of the same nature as the nucleus.

(3.) That the nucleus may remain growing slowly in the solution, becoming increased by a deposition of the salt of the same nature as the nucleus.

B. When the mixture consists of two isomorphous salts.

(1.) Sudden crystallisation may occur, giving a deposition of both salts, apparently in the proportions in which they exist in solution.

(2.) That when slow crystallisation takes place, the nucleus increases by a deposition of the least soluble salt, showing that in mixed supersaturated solutions a gradation of phenomena may be experienced, passing from those shown in the crystallisation of a true supersaturated solution to those shown in the crystallisation of an ordinary saturated solution.

XXVII.—*Quantitative Assay of the Ores and Compounds of Mercury by the Blowpipe.*

By George Attwood, F.G.S., Assoc. Inst. C.E., F.C.S., M. Am. Inst. M.E.

The compounds to be examined are divided into three classes, and will be called A, B, C.

Class "A."

Consisting of metallic mercury.
" cinnabar (artificial state forms what is called vermillion).
" tiemannite (selenide of mercury).
" suboxide.
" protoxide.
" mixed sulphides, &c.

Class "B."

Consisting of calomel (subchloride).
" chloride of mercury (corrosive sublimate).
" iodide of mercury.

Class "C."

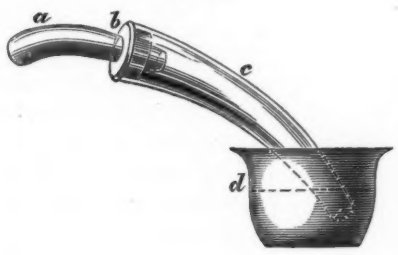
Consisting of amalgams of gold, silver, copper, lead, zinc, tin, &c.

Class "A."—The assay is conducted as follows:

Reduce the ore to a fine powder so that the sample to be assayed will all pass through a sieve of 2,000 holes to the linear inch, weigh out from 10 to 20 grains of ore according to its richness, intimately mix with 5 to 10 times its weight of finely powdered litharge, and distil in a small glass retort over the spirit lamp.

Retorts of the following size and shape (see Fig. 1) have been found to give very accurate results, and can be made by the operator from hard flint glass tubing, by closing one end over the lamp and then bending it, when heated to the required angle.

Fig. 1.



The retort (*a*) or cup is made $\frac{3}{4}$ inch in length, and neck (*b*) of same $\frac{3}{4}$ inch, and $\frac{1}{4}$ inch in diameter. The neck is fitted into a good tight cork and placed firmly in the top of a glass tube (*c*) of about $2\frac{1}{2}$ inches in length, and $\frac{6}{10}$ of an inch in diameter, tapering at the bottom to quarter of an inch. The tube is also bent slightly to facilitate the collection of mercurial vapour in the receiver (*d*). The end of the tube is kept immersed during the heating of the assay in a small cup or capsule containing water, and as the operation occupies only a few minutes, the retort and condensing tube can be held with a pair of wooden tongs without any inconvenience.

Before the retort is used, expel all the moisture by a thorough drying. The above shaped retorts are easily charged by pouring in the ore and litharge from a small mixing spoon, and then connecting it, by means of the cork, with the condensing tube.

The retort is heated very gradually at first over the spirit lamp, and finally the heat is raised until the assay is fused and the glass softens and nearly melts. The greater portion of the mercury will be found in the receiving cup, but small particles will generally be found in the condensing tube; heat the tube slightly, which has the effect of bringing the minute globules of mercury together, then remove them carefully with a feather, and add them to the globules in the cup. The retort and its fused contents should now be broken up in a horn spoon or porcelain dish, on which a small quantity of water has been previously added, and after vanning, examine carefully with a magnifying glass to see if any globules can be found. If they are, the assay should be repeated.

Slightly heat the receiving cup over the lamp, taking care to have it half full of water. The fine globules of mercury will then unite into one globule. Pour off the water and dry the mercury with blotting paper, and remove to a small horn weighing cup, and ascertain its weight on the balance. The mercury so obtained can be considered pure.

FIG. 2.

Class "*B.*"—Cannot be reduced by litharge alone, and a different reducing agent as well as shaped retort must be employed.

Take of the finely powdered ore or product 10 grains, and mix it with about 3 times its volume of neutral potassium oxalate, and one volume of potassium cyanide, and distil in a retort of the following description. See Fig. 2. A small bulb-shaped retort (*a*), constructed of thick hard flint glass about $\frac{1}{2}$ inch in diameter at its widest part, and $\frac{3}{4}$ inch in depth;

length of neck (*b*) about $\frac{3}{4}$ inch; diameter of the latter about $\frac{3}{4}$ inch. The neck is fitted with a good cork and placed firmly on the top of a glass tube about $2\frac{1}{2}$ inches in length, and $\frac{6}{10}$ths of an inch in diameter at the top, tapering at the bottom to $\frac{1}{4}$ of an inch.

The mixture having been placed on the retort, the heat is applied very slowly and with great care at first to avoid the rapid reaction which would otherwise take place. The distillation occupies only a few minutes, and the assay should be completed and the mercury collected and weighed with all the precautions mentioned in Class "A."

Class "*C.*"—Native and artificial amalgams as well as dentists' products are often so hard and compact, as well as mixed with lead, bismuth, zinc, copper, &c., that a correct determination cannot be arrived at by direct distillation, owing to the swelling, spitting, and spurting that takes place soon after the application of heat. An approximative test should be made on charcoal or in a small crucible or glass tube, and if the spurting is found to be so violent that the amalgam cannot be distilled without loss, it should be crushed up in the agate mortar and then placed in the retort for distillation. In many cases the latter plan is most difficult, and in some impossible, without losing a large portion of the sample. In such a case weigh out one equal part of pure mercury, mix it with the assay sample, and then crush it in the agate mortar. The amalgam will then be found to be in a semi-fluid condition, in which state remove it to the iron retort, and the mercury can be evaporated and collected without danger of loss in spitting, and the weight of the mercury added *deducted* from the total found.

In assaying amalgams make two assays.

1st. Distil the amalgam, then condense and collect the mercury and weigh.

2nd. Subject the amalgam to the blowpipe flame either in an open cup or dish, and take the loss of weight to be mercury. The heat never to be sufficient to fuse the retorted metal, else a loss will arise from the volatilisation of lead, zinc, silver, &c., all of which are frequently found combined with mercury.

The last method will be found to be very accurate when the amalgams consist of nearly pure silver or gold combined with the mercury, but if other metals exist with them, the results are very uncertain. It serves, however, not only as an approximate assay, but as a check on the distillation assay.

The retorts used for the determination of the amount of mercury contained in amalgams must be constructed differently from those which are used for Class A and B, and are best made of cast steel, which is afterwards turned in the lathe to the required form.

The retort is made one inch in height, which includes the cup and cap.

The neck, about 2 inches in length, having a gentle taper towards the end, which is made to fit into a good cork, and which has been previously placed in the glass condenser (see Fig. 3).

Fig. 3.—Cross section of the Steel (amalgam) Retort with Glass Condenser.

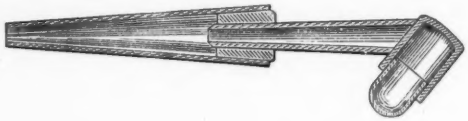


Fig. 4.—View of the Cap and Distillation Pipe of the Amalgam Retort.

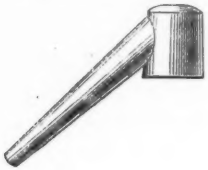


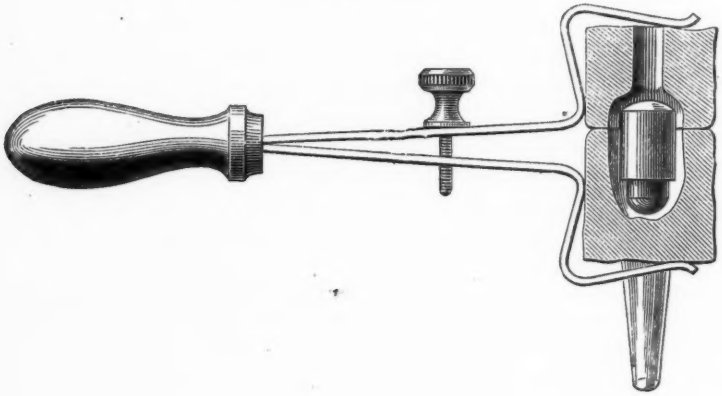
Fig. 5.—View of the Receiving Cup of the Amalgam Retort.

Fig. 6.—View of the Glass Condenser.

10 to 30 grains of the amalgam to be examined are weighed, wrapped up in a small piece of tissue paper, and (the weight of ash contained in a similar piece of the same paper must always be determined in a quantitative assay) placed in the receiving cup (Fig. 5). The cap is now placed firmly on. The joint being perfectly air-tight, no luting is necessary.

The condenser (Fig. 6) is now attached, and the retort placed in

Fig. 7.—A side view of the Holder and Charcoal Furnace, showing end of Retort.



the charcoal furnace, which has now to be held firmly by the holder (see Fig. 7).

The furnace is now brought near the blowpipe lamp, and the end

FIG. 8.—A TOP VIEW OF THE CHARCOAL FURNACE AND HOLDER.

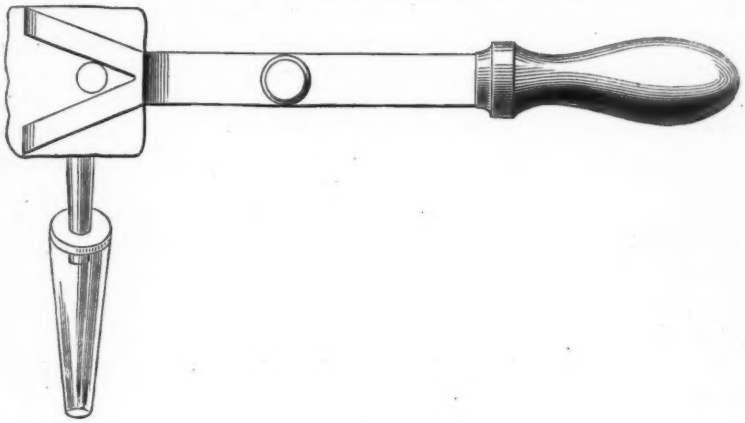
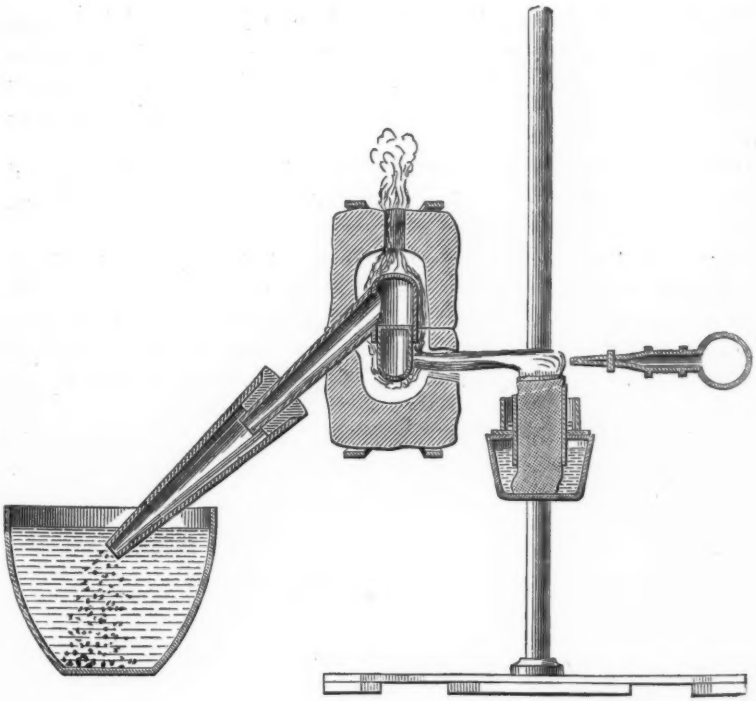


FIG. 9.



of the condenser kept immersed in water contained in a small porcelain crucible.

The heat is applied very quietly at first, but in a few minutes a strong reducing flame may be applied through the hole in the lower part of the furnace.

Flames will soon be seen coming out of the top hole of the furnace, and the retort will be found to be red-hot; keep it so for about two minutes, then cease blowing, and allow the retort to cool.

See Fig. 9. Sectional view of blowpipe stand and lamp, with flame playing on the amalgam retort, which has been placed in the charcoal furnace; also a view showing the position of the condenser and receiver of the mercurial vapour.

The whole operation does not take ten minutes, and although the retort may appear large, the operator will find no difficulty even in obtaining a white heat if necessary, and in a few minutes.

The mercury is collected and weighed according to the methods laid down in Class A.

Most accurate results will be obtained by following the above instructions.

In the assay of *Class A.*—Litharge having been added in excess, readily oxidises sulphur and selenium, and the nature of the matrix does not interfere with the assay. Excess of litharge also prevents arsenic, antimony, and pitchy compounds interfering with its accuracy.

Class B.—Iodides as well as chlorides of mercury are decomposed when heated with both oxalate of potash and cyanide of potassium, leaving a metallic mercury.

Class C.—Assays of amalgams. Apparently it seems easy to determine the quantity of mercury in a sample by heating the same to redness, and then estimating the loss in weight to be mercury; but practice, especially in mixed amalgams, proves the assay to be incorrect, owing to the volatilisation of the baser metals contained in the amalgam.

(The three different retorts, also charcoal holder, all originally designed by the author, were made by L. Casella, 147, Holborn Bars, E.C., where similar ones can now be procured.)

XXVIII.—*On some Points in the Analysis of Combustible Gases, and in the Construction of Apparatus.*

By J. W. Thomas.

The analysis of gas by the aid of the improved forms of apparatus, and the application of the best suited reagents, has of late years attained great accuracy, and its performance is conducted with comparative rapidity. It is unnecessary to enter into detail respecting the various forms of apparatus, or to describe Mr. McCleod's modification of Messrs. Frankland and Ward's, with which some of the determinations herein recorded were made. After working for some time with this apparatus, I noticed, in common with others, that it was not as sensitive as desirable when small volumes of gas were under manipulation, and I have for years turned my attention to the task of devising an apparatus of greater delicacy. I have succeeded in doing this without much altering the form of the apparatus—the fundamental basis of which is the closed pressure tube or barometer tube, devised by Dr. Frankland. As the carrying out of the experiments on the explosion of combustible gases by the aid of diminished pressure alone, without adding excess of hydrogen, oxygen, or air to modify the force of the explosion, led to the alteration of the apparatus, I will describe them first. In the early part of 1874, I observed on several occasions that when a small quantity of marsh-gas was mixed with about three times its volume of oxygen and rarefied (in the eudiometer of McCleod's apparatus), so that the mixture was under a pressure of only 160 mm. of mercury, no explosion took place when a spark was passed. I afterwards tried marsh-gas mixed with twice its volume of oxygen, and found that when the mixture supported only 130 mm. of mercury, the electric spark would not ignite it. Sir H. Davy (*Phil. Trans.*, 1817) states that detonating gas ($H_2 + O$) will not explode when rarefied to $\frac{1}{15}$ of its ordinary density. As marsh-gas mixed with twice its volume of oxygen would not explode when rarefied to $\frac{1}{6}$ of its density, and finding subsequently that electrolytic gas would not explode under the same conditions, it became evident that the cooling effect of the walls of the eudiometer was the chief agent in modifying the force of the explosion. Another point noticed was that the expansion of a gas to twice its volume lessened the force of the explosion to a greater extent than by the addition of an equal volume of inert gas at the initial pressure. In order to take advantage of this effect of rarefaction in the analysis of combustible gases, and to determine whether

complete combustion ensued when a spark was passed in a mixture containing one volume of marsh-gas and two volumes of oxygen, which was so rarefied as to ensure the safety of the eudiometer, I made some gas which gave from the mean of three analyses conducted in the usual manner by exploding with seven volumes of oxygen, 99·81 per cent. marsh-gas.

The following figures of the analyses in detail are given to show the volume of oxygen used; and the "pressure under which the gas was exploded" means the height of the column of mercury in the pressure tube above that in the eudiometer.

Observed pressure of gas.	Temperature.	Corrected vol. at 15·4°.	Progress.
118·5	15·4	118·5°	Volume employed.
357·8	15·4	357·8°	Volume after adding oxygen.
121·2	15·6	121·12°	Volume after explosion.
2·8	15·7	2·8°	Volume after CO_2 absorbed.

Found 99·85 per cent. of marsh-gas.

The pressure under which the gas was exploded was 163 mm. of mercury.

Observed pressure of gas.	Temperature.	Progress.
121·0	14·6°	Volume of marsh-gas employed.
375·1	14·6°	Volume after adding oxygen.
132·9	14·6°	Volume after explosion.
12·1	14·6°	Volume after absorbing CO_2.

Found 99·83 per cent. of marsh-gas.

The pressure under which the gas was exploded was 160 mm.

Observed pressure of gas.	Temperature.	Progress.
139·4	14·0°	Volume of marsh-gas employed.
450·3	14·0°	Volume after adding oxygen.
172·0	14·0°	Volume after explosion.
32·9	14·0°	Volume after absorbing CO_2.

Found 99·78 per cent. of marsh-gas.

The pressure under which the gas was exploded was 169 mm.

Two other analyses of the same gas exploded under 170 mm. and 173 mm. pressure gave respectively 99·91 and 99·93 per cent. of marsh-gas. The explosion under the latter pressure was too powerful, about 160 mm. being the most suitable. Experiments were next tried with mixtures of oxygen and hydrogen in nearly the proportions to form water. The following figures illustrate the results obtained, and the pressure under which the gases were exploded. The oxygen and

hydrogen employed were found to be pure by experiments in presence of excess of hydrogen.

Observed pressure of gas.	Temperature.	Progress.
149·6	13·0°	Volume of oxygen employed.
452·7	13·0°	Volume after adding hydrogen.
4·0	13·0°	Volume after explosion.

The oxygen present was 149·6 volumes, the oxygen found was 149·56 volumes. The pressure under which the gas was exploded was 168 mm. of mercury.

Observed pressure of gas.	Temperature.	Progress.
122·0	13·6°	Volume of oxygen employed.
381·0	13·6°	Volume after adding hydrogen.
15·3	13·6°	Volume after explosion.

Oxygen present 122·0 volumes, oxygen found 121·9 volumes.

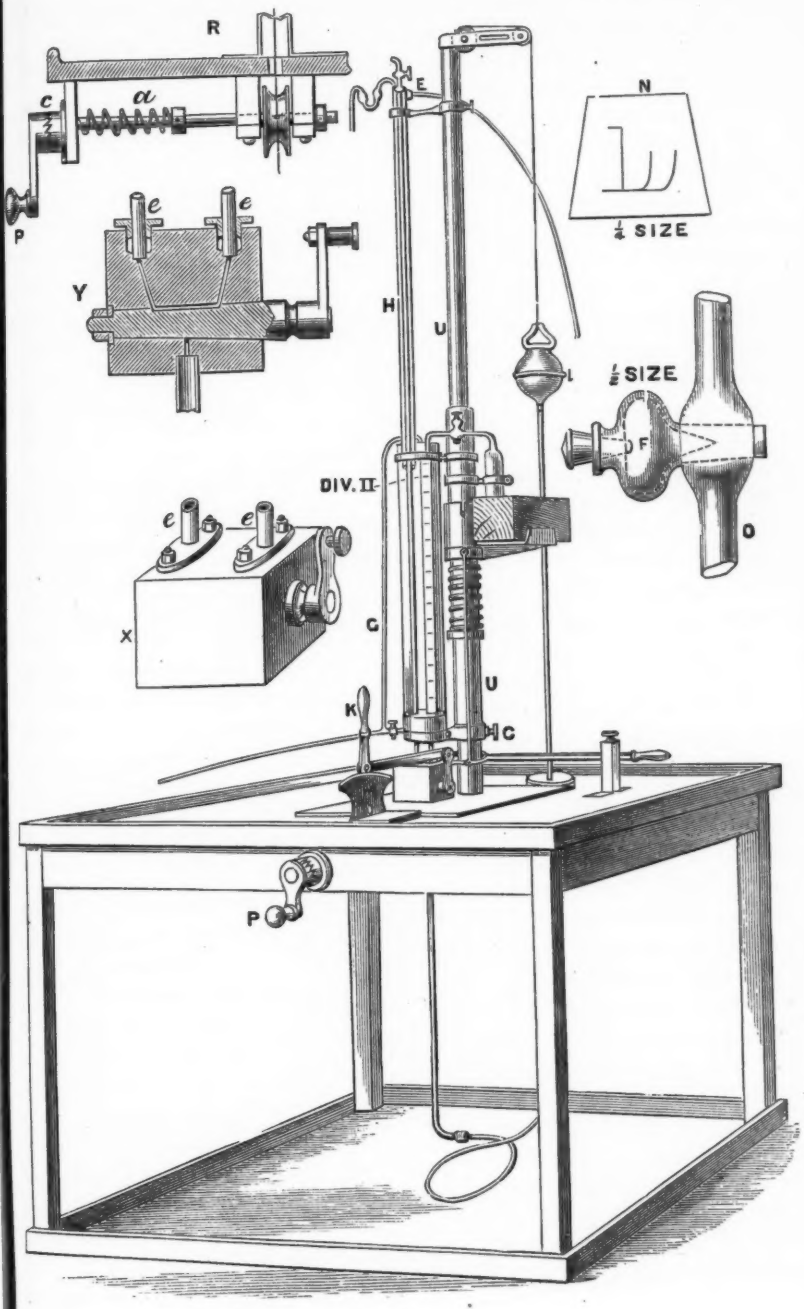
The pressure under which the gas was exploded was 173 mm.

Various other analyses of gaseous mixtures were made both by adding excess of oxygen to modify the force of the explosion, and with little more than was sufficient for complete combustion, and the violence of the explosion simply lessened by considerably rarefying the gases, and the results obtained were very trustworthy. I almost invariably found, however, that the figures were more concordant, and that it was more easy to obtain two or three like results in analysing combustible gases, by exploding under reduced pressure alone, than by the addition of large volumes of oxygen or other gas to modify the violence of the explosion. This was, doubtless, due to the circumstance that when a combustible gas was analysed in McCleod's apparatus—say marsh-gas for instance—the addition of seven volumes of oxygen for explosion would entail the use of a small number of volumes of marsh-gas. In fact if the pressure tube stood as it does in the greater number of apparatus on Dr. Frankland's or Professor McCleod's model, at not more than 350 mm. above Div. 2, only some 20 volumes of marsh-gas could be taken, and the subsequent removal of the large excess of oxygen used to modify the violence of the explosion, leads to the introduction of other large volumes of hydrogen to get rid of the oxygen, and all the errors incidental to the manipulation and to the traces of impurity which the oxygen and hydrogen contain would be thrown upon the small number of volumes of marsh-gas. The employment of a large volume of gas for analysis, which after all registers but a small number of reading volumes, sensibly interferes with the delicacy of the apparatus, especially when it often happens that the quantity of gas at command is small. Before referring further to the analysis of combustible gases, it will be best to notice

the alterations in the apparatus for gas analysis by which that on Dr. Frankland's or McCleod's model may be rendered better adapted and more accurate in the analysis of small volumes of gas. Let the two tubes A B represent, A the barometer tube and B the eudiometer of either Dr. Frankland's or McCleod's modification. The barometer tube is longer than the eudiometer in both instances, but it will answer the present purpose better for description to have them of the same length. There is one c.c. of air above the mercury in the top of B, the remainder of the apparatus being full of mercury and connected at C with the tube of the ordinary mercury reservoir. The mercury reservoir will have to be lowered down nearly 760 mm. below the summit of A before there will be a sensible vacuum in A, consequently the one c.c. of air in B will be placed under the expanding influence of nearly 760 mm. of mercury before a chance is offered for a reading to be obtained off the barometer tube A. If the eudiometer is a narrow one, as in Dr. Frankland's apparatus, the one c.c. of air expanded—say 10 times—will occupy much more length of tube than will the same quantity of air in an eudiometer of about double the internal diameter, as in McCleod's, and the smaller the quantity of air or gas introduced into either apparatus, the more will it become rarefied, because it will remain under the expanding influence of a longer column of mercury. In order to allow of further volumes of gas being admitted for the purpose of exploding or otherwise the mercury will have to be brought down much lower in A, which implies a further considerable rarefaction of the air in B, so that a small quantity of gas would have to be expanded to 20 or even 30 times its original bulk before it could be measured at a workable division. It has often been asserted in reference to these forms of apparatus that the gas is thus placed under like conditions to that in a Bunsen eudiometer; this is doubtless a fact, but the recorded volumes of gas in the two eudiometers are most essentially different. The expansion of a small volume of gas in a Bunsen eudiometer of 800 mm. in length, so that 150 mm. are occupied by the rarefied gas, means a very considerable reduction in the errors of reading, temperature, &c., but the gas in the eudiometer of the apparatus under consideration is not measured therein, as the volumes are recorded from the barometer or pressure tube, and the expansion of the gas in this apparatus leads to error instead of accuracy. The gas in the eudiometer is measured by the column of mercury which it is capable of supporting, and if it is expanded, as it often is in the apparatus mentioned, to 20 or even 30 times its original volume, the errors incidental to the performance of analysis must be augmented materially, and in dealing with small quantities of gas the analyses are not accurate.

In order to obtain the best results with these forms of apparatus when working with explosive gas, it is necessary to use as large a volume as possible, and this necessitates the measuring of the gas at a low division on the eudiometer, so that there may be sufficient vacuum length in the pressure tube to admit oxygen or other gas used in large excess for explosion. When the gas is somewhat rarefied for explosion the eudiometer is in many instances almost filled with the gas under reduced pressure. It appears necessary, therefore, in order to work the usual process of analysis, that the eudiometer should be 800 or 900 mm. in length. The chief point in gas analysis is to have an apparatus which shall register the largest number of volumes, no matter how small the quantity of gas used. The number of volumes is represented by the number of mm. of mercury which the gas supports: hence it is evident that the sensitiveness of the apparatus will depend upon the length of the pressure tube standing *above* the eudiometer. To lengthen the barometer tube of an apparatus having an eudiometer 800 or 900 mm. in length would be somewhat impracticable. It is only when combustible gases are under analysis that the eudiometer is nearly filled, and by dispensing with the excess of oxygen or hydrogen added to modify the violence of the explosion, and resorting to reduced pressure alone to bring about this result, the necessity for so long an eudiometer ceases. By shortening the eudiometer, 500 volumes or more can be read off with a pressure tube having 1,000 mm. graduations, or 700 volumes may be registered by a small quantity of gas in apparatus having a barometer tube 1,200 mm. long, as in McCleod's. In order to render the apparatus very sensitive in the working of small volumes of gas, the barometer tube should be of such length above that of the eudiometer, that when the level of the mercury in the reservoir L on the accompanying figure, would be equal to Div. 1 on the apparatus, there would be a vacuum in the pressure tube—the barometer tube would be thus more than 700 mm. above the shoulder of the eudiometer. An addition of 300 or 400 mm. to the length of the barometer tube of Dr. Frankland's or Professor McCleod's apparatus would render it unwieldy as to height. Having observed, however, that less eudiometer room was required by using the reduced pressure method for explosion, and that much of the eudiometer was taken up by the gas being expanded before a vacuum was obtained in the pressure tube, I reduced the eudiometer to rather less than 500 mm. from shoulder to shoulder, and found that there was then practically more space at command than before, because the original volume of gas does not require to be much expanded before a reading can be taken, and thus a smaller quantity of gas registers more actual volumes than a much larger quantity with the long eudiometer. Some of the heaviest hydrocarbon gases (C_4H_{10} for instance)

have been analysed, using a volume giving a reading of 80 volumes or more, and less than one half of its length (500 mm.) has even been occupied by the gas rarefied for explosion, so that it could be shortened to 400 mm., and still afford ample length for working with any explosive gas. I used this form of apparatus, having a large pressure tube and short eudiometer, for about two years, and found it to answer admirably. As soon as I adopted the short eudiometer, it became evident that there was one serious objection to the long column of the barometer tube above the eudiometer, as it entailed the lowering of the mercury reservoir with great care. This was owing to the mercury in the pressure tube descending and producing a vacuum, and then, if from any cause the gas from the laboratory tube came over suddenly, it enabled the mercury to rush up and seriously endanger the safety of the tap at the upper end of the barometer tube. To obviate this a tap would have to be placed at the lower end of the barometer tube, for the purpose of cutting off the communication when the gas was being transferred from the laboratory tube to the eudiometer, and as I had often experienced some difficulty in keeping the india-rubber connections and glass taps at the lower end of the eudiometer and barometer tubes in good condition, the introduction of another tap would add to the complications. Moreover, another difficulty I experienced was that the corresponding level of the mercury in the barometer tube with the divisions on the eudiometer could not be relied upon, owing to the tendency of either tube to lower by the weight of mercury contained in it, and by the continual vibration of the apparatus during manipulation. I succeeded in devising a tap which does the work of the three required, and have overcome the objections enumerated. By the introduction of a steel block in which the tap—itself of steel—works (details X, Y, in figure), the glass taps and connections are dispensed with, while the usual cut-off, supply, and the additional communication with the barometer tube are obained. The lower end of the eudiometer is simply a neck of the same outside diameter as that of the barometer tube, viz., $\frac{3}{8}$ of an inch, and after rounding off the edges in a blow-pipe flame, the tubes are slipped into two sockets furnished in the steel block, which is $2\frac{3}{4} \times 2\frac{1}{2} \times 2$ inches thick. The sockets, *e e*, are $\frac{3}{4}$ inch diameter in the top, and in the bottom, for $\frac{1}{4}$ inch in depth, only slightly larger in diameter than the glass tubes. Two glands (ordinary engine cylinder gland pattern) are screwed down firmly on the india-rubber packing used to make the joint. Two or three india-rubber rings $\frac{3}{8}$ of an inch diameter and about $\frac{1}{4}$ inch thick, are slipped on either tube. The two tubes are then lowered into the sockets in the steel block, which is firmly fixed to the table, as shown in the drawing, and the glands screwed down upon them. A thorough tight joint, which is unaffected by the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temperature as the other caoutchouc connections are, is thus afforded. The barometer tube on my apparatus has been for 22 months in the socket, and not attended to during the interval. The advantage of this arrangement is that there is no rigidity given to the tubes, because a full $\frac{1}{16}$-inch play is allowed inside the glands, while the corresponding levels must remain the same, as the tubes cannot possibly lower, and the liability of fracturing the barometer and eudiometer tubes by clamping to maintain them in position is entirely obviated, because the clamp C is simply used to support the water cylinder. No holes are drilled in the steel plug, but by the aid of a sharp gouge, grooves are cut which communicate with the holes drilled in the block. The detail of the tap Z represents a sheet of paper which exactly covers the circumference of the plug, opened out so as to show the manner in which the grooves are cut and the position they occupy. The tap spindle is cranked in order to be under control from a point at the margin of the table or where the telescope is fixed. As shown in the figure, the crank of the tap is joined by means of a connecting rod with the handle K, the bearing of which forms a quadrant M, so graduated as to show the exact positions of the communications which the tap affords. By means of the quadrant the tap can be regulated to the greatest nicety, and the last portion of gas from the laboratory tube may be brought over so slowly that the absorbent can be admitted into the capillary tube to any point required. The tap performs four separate offices, but these are easily found out, and need no description.

Some twelve months ago I endeavoured to simplify the communications between the laboratory tube and the eudiometer, with a view to dispense with the steel facets and clamp, and to remove the necessity of disconnecting the laboratory tube from the eudiometer during an analysis. I have succeeded in doing this in a simple manner, using only one glass tap instead of the two, and doing away with the clamp altogether. The laboratory tube, as shown in the figure, is joined to the eudiometer by a continuous capillary tube of much larger outside diameter (10 mm.) than that used in Prof. McCleod's apparatus. The difficulty to be overcome, without disconnecting the laboratory tube, was the removal of the absorbent from the capillary tube when the gas was transferred to the eudiometer. This is done in the apparatus figured, by means of the tap F (shown half size at O), which is hollow in the centre, having a way communicating with the capillary tube leading to the laboratory vessel. The tap F has two ways, one a through way between the eudiometer and the laboratory tube, and the other a way leading into the hollow of the tap, by means of which either the eudiometer or the laboratory tube may be washed out. When an analysis is being done, the hollow in the tap F is nearly filled with mercury, and a small stopper is inserted in order to cut off

communication with the atmosphere when the laboratory tube does not require washing out. If an absorption is going on, the mercury, which is caused to drop through the gas, may be supplied through the hollow in the tap, or from the eudiometer. The laboratory tube on the figure being permanently joined to the eudiometer, requires supporting, on account of the necessity to remove the mercury trough for the purpose of washing out the laboratory tube. This is accomplished by the clamp which is fixed to the upright, U. In order that the mercury trough may be moved out of the way to wash the laboratory tube, the spiral spring on the support, U, is compressed by means of tension rods, as shown. In the guide of the table holding the mercury trough there is a slot which runs up against a stud in the upright to keep the trough in its right position; and when the latter is depressed by the tension rods acting on the spiral spring, the slot is brought below the stud, and the top ferrule holding the guide rods being movable, the trough can be turned round out of the way, leaving the laboratory tube in a position to be easily washed out by a syringe. I prefer supporting the laboratory tube during manipulation by the clamp D, to its resting on the trough, which, however, can be nicely adjusted by the screw in the top of the lever guide. In either case it will be found that the whole apparatus will vibrate sufficiently to cause the absorbent in the laboratory tube to be thrown against the sides thereof.

Owing to the sensitiveness of the apparatus as figured, I experienced some difficulty in maintaining the temperature sufficiently even. It will be seen that the greater length of pressure tube above the eudiometer requires special attention, because the tension of aqueous vapour varies with the temperature, and the vacuous space above the mercury in the barometer tube must be kept at an even temperature. After some trials I found the following arrangement to answer best. The water from the main is run in at the top of the casing tube of the barometer, E (where the water is drawn off in McCleod's apparatus), and the colder water being heavier than that in the water cylinder, finds its way down to the bottom. There is a tap in the cork at the bottom of the cylinder, and to the exit tube from this ($\frac{1}{8}$ inch in diameter) is joined the vertical tube, G, which is bent over on the upper end, in order that it may reach $\frac{3}{8}$ of an inch below the top of the water cylinder. The water from the cylinder is allowed to drop slowly through the tap at the bottom, and in doing this it sucks air through the upright tube communicating with the top of the water cylinder, and in this manner the upright tube G is converted into a self-acting syphon, which draws off the water at the top of the cylinder as soon as it rises to the orifice. This arrangement acts admirably, a strong current of water being drawn off without any fear of the

water running over the cylinder. The casing tube of the barometer, H, should be as wide as possible.

The windlass for raising and lowering the mercurial reservoir, L, is fixed under the table, the cord passing over the pulleys and down the hollow iron support, U (which is made of gas pipe 2 inches in diameter from the bottom to the top of the water cylinder and $1\frac{1}{4}$ inch diameter above that point). The detail R shows the arrangement. The handle, P, is under the command of the operator, as it is in front of the apparatus, and the spring ratchet movement allows the reservoir to be raised or lowered by one hand. The spiral spring, *a*, draws the ratchet, *c*, in gear when the outward pressure is removed.

Since I have adopted the combined eudiometer and laboratory tube as figured, my apparatus is of the following dimensions. The eudiometer is 450 mm. from shoulder to shoulder, having the capillary tube very abruptly joined on, and the wires sealed close to the top, so that Div. 1 is only 12 mm. from the shoulder, and not more than 5 c.c. capacity. It has marks throughout, 20 mm. apart. The first graduation on the barometer tube is about 20 mm. from the top of the cork in the water cylinder, and from thence there are 1,000 mm. divisions, so that there are 640 mm. divisions above Div. 1 on the apparatus. The whole length of the barometer tube is about 1,100 mm. This apparatus gives very good results, and as the smallest quantity of gas can be analysed by it, I think it would not be advisable to lengthen the barometer tube, because there would be more difficulty experienced in keeping the temperature uniform.

When a small quantity of gas is to be analysed for combustible gases, say $\frac{1}{2}$ c.c. for instance, it is necessary to sweep out the capillary tube after transferring the gas (mixed with oxygen or hydrogen) with a small bubble of oxygen or hydrogen, as the case may be. This is done by introducing a small bubble into the laboratory tube, and drawing it over into the eudiometer. This precaution is very essential, because the amount of gas left in the capillary and in the way of the tap would not be exploded, and would thus introduce appreciable error. The volume of gas in the tap-way and capillary tube is somewhat less in this form than in the detachable laboratory tube and eudiometer of Regnault's apparatus, and the same precaution should be observed in analysing small volumes of gas in Dr. Frankland's or McCleod's apparatus.

The following is a brief outline of the method I adopt in dealing with explosive gases in the apparatus having a short eudiometer, without adding much excess of inert gas to modify the force of the explosion. In an analysis of coal gas, for instance, 200 or 250 volumes (measured at Div. 2) are employed. After the absorptions are performed, the remaining gas (200 volumes or more) is used *in toto* for

the determination of hydrogen, carbonic oxide, and marsh-gas. One and a half times as much oxygen as the volume of the gas is introduced into the laboratory vessel, and a current of mercury passed through the gas for a minute in order to mix it; then transferred to eudiometer, measured, and the pressure reduced to 180 mm. of mercury, and the gas exploded. After absorbing the carbonic acid formed, $2\frac{1}{2}$ times as much hydrogen as the volume of the remaining gas is added, the volume determined, and the pressure of the gas reduced to 170 mm. of mercury, and the gas is then exploded. After reading off the volume the first portion of the analysis is completed. To determine the percentage composition of the C_nH_{2n} gases, 200 vols. measured at Div. 2 are used. About twice as much oxygen is added, the volume determined, and the pressure of the gas reduced to 180 mm. of mercury, and the spark passed.

In order to discover the nature of a gaseous mixture, the composition of which is unknown, the method I adopt is the following. The quantity of gas used will depend upon the supply at command, but should not exceed 80 vols. measured at Div. 2. The usual absorptions are first performed, and 5 vols. of oxygen added. The pressure is then reduced to 130 mm., in other words, the gas is expanded until it supports only 130 mm. of mercury, and the spark passed. If no explosion takes place, the barometric column is raised to 160 mm., and no explosion resulting, to 190 mm., then to 250 mm., then 400 mm., then ordinary atmospheric pressure, and, lastly, the gas is placed under as much pressure as can be obtained by raising the reservoir to the top of the apparatus. If no explosion happens under these conditions, about 100 vols. of hydrogen are added, and the pressure of the mixture reduced to 200 mm. of mercury. If no explosion takes place when the spark is passed, the gaseous mixture is placed under ordinary atmospheric pressure and exploded. If no carbonic acid is formed, and two-thirds of the contraction due to the explosion is equal to the volume of hydrogen added, the absence of hydrocarbon gases and hydrogen may be inferred. If, however, the gas should consist entirely of ethyl—a circumstance of rare occurrence—by following the process mentioned it would explode under a pressure of 200 mm., and carbon would be deposited in the eudiometer (owing to incomplete combustion). If such heavy hydrocarbons are suspected, add 7 vols. of oxygen, and reduce the pressure to 130 mm. of mercury. By working this method the safety of the eudiometer is ensured, and the large number of volumes which a bubble of gas may be made to register adds to the accuracy of the analysis. If a mixture is known or found to consist for the most part of marsh-gas, about $2\frac{1}{2}$ vols. of oxygen are added, and the exploding pressure is 170 mm.

The exploding pressure for olefiant gas mixed with $3\frac{1}{2}$ vols. of

oxygen is 130 mm., and for hydride of ethyl with 4 vols. of oxygen the exploding pressure is 120 mm., which will be found to be sufficient expansion for any other hydrocarbon gas. The exploding pressure of hydrocarbon gases containing two or more atoms of carbon in the molecule does not vary much. This is owing to the large volume of oxygen which they require for complete combustion, and to the fact that a very small quantity of gas mixed with 4 or 6 vols. of oxygen, and expanded to five times the volume, will occupy a long column in the eudiometer, and consequently be exposed to a considerable cooling surface. The exploding pressures given are those determined and used with an eudiometer having an internal diameter of about 19 mm. If, therefore, the internal diameter of any eudiometer be much less than this, a mixture will not require to be so much expanded, and if of much greater diameter a mixture will have to be rarefied to a greater extent in order to ensure the safety of the eudiometer. The eudiometer of gas apparatus now generally made are about 20 mm. internal diameter, and the examples given will apply.

In conclusion, I would express my deep obligations to Dr. Frankland for his valuable assistance and advice.

XXIX.—*The Isomeric Dinaphthyls.*

By Watson Smith.

The objects of this investigation were the following:—

I. *To prepare a quantity of the αα-dinaphthyl melting at* 154°, *by Lossen's method, in order to compare it with the body which I obtained in yellowish plates and melting at* 147°, *in company with the other two isomerides, ββ and αβ, so as to be quite sure of the identity of these bodies* (see Chem. Soc. J., 1877, ii, 551—565).

II. *To examine the crude product obtained by Lossen, in order to see if it contained, besides the dinaphthyl αα, any of the other two dinaphthyls in appreciable amount.*

III. *To prepare sufficient quantities of the three isomerides in perfectly pure condition, and to make determinations of their vapour-densities, and so establish their molecular weight.*

IV. *To discover further reactions in which dinaphthyl is formed, so as to find out, if possible, so much about the conditions of its formation as would lead to a method of preparation more easily*

carried out, and giving a larger yield of product, than the present method with antimony trichloride.

I. Lossen, in the preparation of the $\alpha\alpha$-dinaphthyl, recommends that powdered manganese peroxide be heated in a retort with sulphuric acid diluted with twice its weight of water. I found it advantageous to use a stronger acid, viz., sulphuric acid with rather more than its own bulk of water; in the other case the reaction proceeds very slowly, and much time is lost. I found it a great advantage also to modify the process of extraction as follows:—After boiling up the contents of the retort with water, and filtering, the residue was boiled repeatedly with alcohol, and each time thrown on the filter. The alcoholic extracts were now mixed, and the alcohol distilled off on the water-bath, till at last it was impossible to proceed, on account of violent bumping of the contents of the distillation flask. This was entirely prevented by the following device, whereby the distillation proceeded as rapidly as could be wished, and very quietly. A gentle stream of air from an adjoining gas-holder was bubbled through the heated alcoholic solution in the flask, the latter being still connected by another tube with the Liebig's condenser. When all the alcohol was driven off, the residue was transferred to a retort with thermometer, and the naphthalene was separated by distillation up to 130°. Some dinaphthyl carried over also was recovered in another distillation. The temperature rises rapidly after removal of naphthalene to over 360°, when dinaphthyl passes over easily as a resinous mass, like "Canada balsam" condensing in the stem of the retort. The blood-red substance accompanying and colouring the product up to this point here separates by passing over as a bright red sublimate. It can easily be caused to deposit itself almost entirely separate, and apart from the treacly-looking dinaphthyl distillate. After a short time this resinous mass begins to set and crystallise. From the residue left after the repeated treatments with alcohol, benzene still extracts a product, which colours it blood-red. On evaporating, a residue was obtained, consisting of a red resin, and the chocolate-brown amorphous powder described by Lossen. This dinaphthyl precisely resembles the $\alpha\beta$-modification in separating from a too concentrated solution in petroleum spirit, &c., in little round warty masses. By recrystallisation, and a final boiling of the petroleum spirit solution with animal charcoal for some time, and filtering, perfectly colourless rhomboidal plates of the dinaphthyl were obtained (m. p. 154—155°). In a paper read before this Society in 1877 (see Journal for 1877, **2**, 560) I stated that the body melting at 147°, which I did not get quite colourless, was to all intents and purposes pure, and therefore the melting-point might be taken as correct at 147°. I found, however, that the

body obtained by the above method of Lossen's precisely resembled that which I described in the paper mentioned in all its properties, so long as it possessed only a faint yellow tint, and even melted at 147—148°. But on boiling with good animal charcoal for an hour or two in petroleum spirit solution, and filtering, and so obtaining perfectly colourless crystals, it was found that these melted at 154—155°. Moreover, though I made a most careful examination, I could not detect the presence of a trace of the $\beta\beta$-dinaphthyl melting at 187° in the reaction-product above mentioned. By this comparison I have convinced myself that the body described in my previous paper, melting at 147°, is really identical with the body obtained as above by Lossen's method, viz., the $\alpha\alpha$-dinaphthyl, and I am sure that had I had sufficient to submit to a prolonged boiling with animal charcoal, and recrystallisation, I should have obtained my product white, and with a melting-point of 154°.

II. In order to find if any of the $\beta\beta$-dinaphthyl is formed together with Lossen's $\alpha\alpha$-substance by oxidising with manganese dioxide and sulphuric acid, the residue obtained on repeatedly washing with alcohol, consisting chiefly of unaltered manganese dioxide, &c., was now treated repeatedly with hot benzene, whereby a deep-red solution was obtained. This solution on evaporation, filtration with animal charcoal, &c., did not yield a trace of the more insoluble and easily crystallising $\beta\beta$-dinaphthyl. The mother-liquors (petroleum spirit) from which the $\alpha\alpha$-dinaphthyl crystallised, and which yielded crystals melting at first at only 142°, were also examined for the $\alpha\beta$-isomeride, but none could be obtained. The benzene solution above mentioned extracts merely a considerably further quantity of the red resinous body, and the so-called chocolate-brown polymer, described by Lossen.

III. The determinations of the vapour-densities of the three dinaphthyls were made with the co-operation of Herr Karl Meyer, Assistant in the private laboratory of Professor Victor Meyer, of the Zürich Polytechnikum. I gladly take this opportunity of thanking Professor Victor Meyer for his kindness in allowing me the use of his laboratory and newly-devised apparatus, during the determinations of these vapour-densities. Considering the very high boiling points of these dinaphthyls ($\alpha\alpha$, little under 440°, $\alpha\beta$, rather lower than $\alpha\alpha$, and $\beta\beta$-dinaphthyl considerably over 440°), and the fact that at their boiling-points they all turn brown, and become slightly decomposed in presence of air, it will be acknowledged that their vapour-density determinations served also as a good and even severe test for the value of Victor Meyer's new method in its wider application. For simplicity and rapidity of execution (the temperature of the lead-bath used not requiring to be known) the method is perfectly admirable.

With regard to the accuracy attainable the numbers speak for themselves.

The three substances were perfectly purified as follows: The $\beta\beta$-isomeride (m. p. = 187°) was boiled for some time in benzene solution with animal charcoal, when on filtering and crystallising, it was obtained in perfectly white plates with a slight blue fluorescence. The $\alpha\alpha$-isomer (m. p. 154°) was treated just like the preceding, but petroleum spirit was used instead of benzene, in which the substance is rather too soluble. Small, delicately white plates, rhomboidal, like the preceding, but not showing fluorescence. In the same manner the $\alpha\beta$-isomeride (m. p. 76°) was obtained in small white plates, six-sided, and apparently a combination belonging to the monoclinic system. They possessed a pearly lustre. On heating the three isomerides a little over their melting points another graduation in properties was observed in addition to those already cited, viz., the $\beta\beta$-substance emits a vapour with scarcely any perceptible odour; the $\alpha\alpha$-isomeride emits a faint but decidedly pleasant aromatic odour; the $\alpha\beta$-isomeride an odour almost exactly like that of the preceding body, but rather more intense. On allowing all three fused substances to cool, another graduation was observed in the times taken to attain their respective solidifying and crystallising points. $\beta\beta$ solidifies immediately on cooling to a crystalline solid mass; $\alpha\alpha$ first forms a resinous mass like Canada balsam in consistency, and then after an hour or so, solidifies to a white crystalline mass; $\alpha\beta$ conducts itself precisely like $\alpha\alpha$, only that it requires at least a day or two, and often more, to crystallise. These observations were made with the substances contained in glass tubes of equal size and diameter. The results obtained in determining the vapour-densities in air at first, were uniformly too low, varying in all three cases from 8·00 to 8·20, as we noticed, too, that the substances were in every case turned brown, and knowing that slight decomposition must result in too low a number, we determined to repeat the determinations in an atmosphere of nitrogen, as recommended in such cases by V. Meyer.

This time most satisfactory results were obtained.

Calculated Vapour-Density for Dinaphthyl ($C_{20}H_{14}$) = 8·77.

The data required from this method are exhibited in the following equation, which gives the density d:—

$$d = \frac{S.760(1 + 0{\cdot}003665t)}{(B - w)V.0{\cdot}001293}$$ where B = height of barometric column at 0°.

Or collecting constants—

$$d = \frac{S\,(1 + 0{\cdot}003665t)\,587780}{(B - w)V}$$

w = tension of aq. vapour for t.
t = temperature of the air in grad. tube.
S = weight of substance taken.
V = volume in c.c. of displaced air.
d = vapour density.

ββ-Dinaphthyl (m. p. 187°).

B=718·3, w=11·908, t=14°, S=0·16175, V=16·2 c.c.

$$d = \frac{0{\cdot}16175\,(1 + 0{\cdot}003665.14)\,587780{\cdot}0}{(718{\cdot}3 - 11{\cdot}908)\,16{\cdot}2} = 8{\cdot}73.$$

αα-Dinaphthyl (m. p. 154°).

(I) B=718·3, w=11·162, t=13°, S=0·15075, V=15·2 c.c.

$$d = \frac{0{\cdot}15075\,(1 + 0{\cdot}003665.13)\,587780{\cdot}0}{(718{\cdot}3 - 11{\cdot}162)\,15{\cdot}2)} = 8{\cdot}64.$$

(II) B=718·3, w=11·53, t=13·5, S=0·1375, V=13·8 c.c.

$$d = \frac{0{\cdot}1375\,(1+0{\cdot}003665.13{\cdot}5)\,587780{\cdot}0}{(718{\cdot}3 - 11{\cdot}53)\,13{\cdot}8} = 8{\cdot}70.$$

αβ-Dinaphthyl (m. p. 76°).

(I) B=718·3, w=12·7, t=15°, S=0·1575, V=15·7 c.c.

$$d = \frac{0{\cdot}1575\,(1+0{\cdot}003665.15)\,587780{\cdot}0}{(718{\cdot}3 - 12{\cdot}7)\,15{\cdot}7} = 8{\cdot}81.$$

(II) B=718·3, w=12·7, t=15°, S=0·14125, V=14·2 c.c.

$$d = \frac{0{\cdot}14125\,(1+0{\cdot}003665.15)\,587780{\cdot}0}{(718{\cdot}3 - 12{\cdot}7)\,14{\cdot}2} = 8{\cdot}74.$$

		Found.	Calculated.
The mean results are then: for	*ββ*-dinaphthyl ...	8·73	8·77
„ „	*αα*-dinaphthyl ...	8·67	
„ „	*αβ*-dinaphthyl ...	8·78	

I may just add that the two determinations of the density of the *αβ*-isomeride were made in one hour and a quarter, including the calculation of the results after each experiment.

IV. The effect of passing naphthalene, together with antimony trichloride and tin tetrachloride, through red-hot tubes having been ascertained, it was next determined to pass through mixtures of naphthalene with certain organic chlorides, such as carbon tetrachloride and chloroform, monobromnaphthalene, &c.

Carbon Tetrachloride and Naphthalene.—The reaction expected was $4C_{10}H_8 + CCl_4 = 2C_{20}H_{14} + 4HCl + C$. A little under the calculated quantity of naphthalene for the above equation was taken, and as much was dissolved, with the aid of heat, in the carbon tetrachloride as the latter would take up. The mixture, kept fluid by warming from time to time, was passed drop by drop into the red-hot tube through a small tap-funnel. At an intense heat almost complete decomposition ensued, with evolution of volumes of black smoke and much hydrochloric acid, at a less intense heat separation of carbon (black smoke), hydrochloric acid gas, and a good yield of dinaphthyl, the $\beta\beta$-isomer chiefly, as with the other hot tube methods. So large a yield with so low a temperature has not been previously obtained. The heat was merely a faint dull red.

Chloroform and Naphthalene.—The experiment was carried out just like the preceding one. Carbon was separated in black smoke and also hydrochloric acid gas, and a distillate was obtained, which was transferred to a small retort. On distilling, first naphthalene passed over, and then at 230° a decomposition ensued with some effervescence, hydrochloric acid gas being abundantly evolved. At length the temperature rose to over 300°, when $\beta\beta$-dinaphthyl accompanied by a yellow sublimate passed over. On purifying, by washing and recrystallisation, it melted at 187°. The decomposition in the tube seemed to proceed much the same as when carbon tetrachloride was used; however, it would appear that chlorine additive naphthalene compounds are formed, which decompose afterwards on distillation. To prove this, in a subsequent distillation in the small retort, I stopped short of the point of distillation when evolution of hydrochloric acid takes place, and then boiled the residue with strong alcoholic potash, to convert any additive into substitution products, which are stable bodies. The alcoholic solution was then evaporated to dryness, and a little of the residue in fine powder was mixed with sodium, and introduced into a glass tube closed at one end, and heated. On subsequent solution in water, chlorine was found on testing with silver solution. The formation of these additive compounds and their subsequent decomposition with evolution of HCl, renders this a less desirable method of preparation.

Naphthalene and Carbon Bisulphide.—As concentrated a solution as possible was obtained, so that it solidified on cooling and required warming to liquefy it. This was passed as before drop by drop,

through the red-hot tube. Small separation of carbon, with evolution of sulphuretted hydrogen also in small quantity. The but slightly decomposed naphthalene came through the tube unusually white, and thus very unlike its appearance even when passed through alone. A little $\beta\beta$-dinaphthyl was formed, and was much freer than usual from other bye-products. At the close of the distillation afterwards in the small retort to separate from naphthalene, &c., a little of the yellow sublimate before noticed passed over. I believe in this case it is quite probable the carbon bisulphide did not assist at all in decomposing the naphthalene, but that rather the hydrogen liberated by the mere action of the high temperature on the naphthalene, served to decompose the carbon bisulphide. The reaction expected was $CS_2 + 4C_{10}H_8 = 2H_2S + C + 2C_{20}H_{14}$. It was noticed that the carbon bisulphide, which before passing through the hot tube, possessed a most disagreeable odour, after passing through and condensing with the naphthalene, had quite lost its disagreeable smell, and now had merely a pleasant ethereal odour.

It was now thought interesting to try to obtain if possible the $\alpha\alpha$-dinaphthyl by passing a mixture of monobromnaphthalene with naphthalene through the red-hot tube. $C_{10}H_7Br(\alpha) + C_{10}H_7H = C_{10}H_7(\alpha) + HBr.$
$|$
$C_{10}H_7(\alpha).$

Naphthalene and Bromnaphthalene.—The calculated quantities were taken, and the naphthalene was dissolved in the monobromnaphthalene, and dropped through the tube as before. There followed a separation of carbon to some extent, though not much, and a considerable evolution of hydrobromic acid gas. The tube was at a bright red heat. On transferring the crude product coming through to the small retort and distilling, naphthalene passes over first, and then at about 230° a decomposition with evolution of hydrobromic acid sets in, which continues as the temperature rises to 280°, when some bromnaphthalene comes over. Finally dinaphthyl-$\beta\beta$ passes over, as in all previous experiments, amid evolution of hydrobromic acid gas. A small mass of coke is left in the retort, as is generally the case. It is then probable that unstable bromine compounds are formed, which decompose on distillation, with copious evolution of HBr, and leaving a charred mass in the retort. Thus not $\alpha\alpha$- but $\beta\beta$-dinaphthyl is formed in the above reaction in considerable quantity, though no doubt minute quantities of both the other isomers are also formed.

The Previous Mixture over Soda-lime.—The disagreeable evolution of much hydrobromic acid in purifying the product by distillation in the last experiment, and also the large amount of coked residue obtained at the end of the process, led me to think the reaction tending

to the formation of dinaphthyl might be supported and aided by interposing a substance in the tube, having a strong attraction for the halogen, and also for the hydrogen. Soda-lime was chosen, because it was thought probable that the following reaction would occur:

$$C_{10}H_8 + C_{10}H_7Br + NaOH = C_{20}H_{14} + NaBr + H_2O.$$

A wide combustion-tube (Bohemian glass) was furnished with a layer of well-dried soda-lime, with which a little lime had been mixed to prevent too easy fusion at the high temperature. In the mixture, somewhat over the calculated proportion of naphthalene was taken. The whole process proceeded most easily and pleasantly, no trace of HBr escaping. A considerable amount of the yellow sublimate so often noticed issued from the tube like yellow smoke, and would not condense so easily as the other products. Very little separation of carbon took place. A mixture of 37 grams of bromnaphthalene and 24 grams of naphthalene had been taken and passed through the tube. On transferring the dark-brown mass which came over to a small retort, to separate the products by fractional distillation as before, only one drop of bromnaphthalene came over at about 280°. The gas-pressure being low at the time of the experiment, a sufficient heat was not obtained, and so the yield, in any case a large one, would have been much greater had a bright red heat only been attainable at the time. The great drawback on the method is that a fresh tube requires to be taken for each experiment, and for the preparation of sufficient quantity of dinaphthyl for any considerable investigation for each renewal of the soda-lime a fresh tube would be needed. A tube of Bohemian glass was taken of about 19 mm. internal diameter.

The Mixture over Lime.—The mixture of naphthalene and bromnaphthalene was now passed over good quicklime (in small lumps) in the red hot tube. No yellow vapours were observed as with soda-lime, and it was easy to see the decomposition did not proceed so well. The dark-brown product was distilled from a retort, when naphthalene and some quantity of bromnaphthalene passed over, and then at length some dinaphthyl. The yield was just a fair one, but not nearly so good as with soda-lime. However, the pieces of lime (containing also combined bromine) were easily removed from the tube after the experiment, and could be renewed, but now the method is no improvement on the method with antimony trichloride. It would thus seem pretty well proved that the —OH group in the sodium hydrate plays an important part in the reaction, as stated in the equation given: $C_{10}H_8 + C_{10}H_7Br + NaOH = C_{20}H_{14} + NaBr + H_2O$.

Bromnaphthalene and Naphthalene over Ferric Oxide.—Reaction ex-

pected: $Fe_2O_3 + 4C_{10}H_7Br + 6C_{10}H_8 = Fe_2Br_4 + 3H_2O + 5C_{20}H_{14}$. The tube was a wide one as before, and was well lined with anhydrous ferric oxide. A bright red heat was maintained throughout. Some decomposition took place with formation of black smoke. A considerable amount of yellow vapours sublimed over. All but a drop or two of bromnaphthalene was decomposed, and on fractionating in the small retort afterwards, the crude brown-black product yielded a considerable amount of $\beta\beta$-dinaphthyl. In this and every experiment in which the hydrocarbon was formed, I need scarcely say it was always obtained afterwards in the pure state, and its melting point taken so as to be thoroughly identified.

The above Mixture over Metallic Silver.—But little hydrobromic acid evolved, and but little decomposition. Tube at red heat.

Bromnaphthalene alone over Metallic Silver.—Tube red hot as before. At first but little evolution of HBr, but when a certain amount of AgBr was formed, a vigorous evolution commenced which was maintained throughout the experiment. It certainly seemed as if the AgBr acted as a carrier, being reduced and giving HBr, and then becoming immediately brominated again, for the evolution became most liberal, after a certain amount of silver was converted into bromide, before which scarcely any gas evolution was to be observed.

By this reaction a heavy oil and a resinous body were obtained, both boiling above 300°, but dinaphthyl was not detected.

I am continuing my researches on the subject, and soon hope to lay more results before this Society.

The above experiments were made in the Laboratory of the University of Zürich, and to Professor Merz I beg to tender my thanks for the kindness he has shown me.

XXX.—*On the Occlusion of Hydrogen by Copper.*

By George Stillingfleet Johnson, Daniell Scholar of King's College, London.

In the Chemical Society's Journal (1876, **1**, 178) the results of some experiments of mine on this subject are briefly recorded. I then arrived at the conclusion that rolled copper wire, when oxidised at the blowpipe and subsequently reduced in hydrogen at a red heat and allowed to cool in the gas, occluded hydrogen to the amount of from ·0063 to ·0077 gram of hydrogen for 100 grams of copper; the hydro-

gen being weighed as water, which was produced by igniting the charged metal in a current of dry air, and absorbed by a V-tube containing pumice moistened with strong sulphuric acid.

I was induced to return to this subject by the appearance of a paper by Dr. Thudichum (published in the Chemical Society's Journal for 1876, **2**, 251), in which he gives the results of some experiments, by himself and Dr. Hake, showing that mere traces of hydrogen are occluded by freshly reduced copper, and that no appreciable error could be caused in organic analysis by the oxidation of such minute quantities of occluded gas.

The results of a number of careful experiments have led me to adhere to the belief that the occlusion of hydrogen by copper *may* be, and probably often is, the cause of serious error on the side of excess in the determination of hydrogen in the ultimate analysis of nitrogenous organic substances.

Dr. Thudichum has pointed out the great discrepancies which exist between various chemists, and even between the analyses of the same chemist, as regards the actual quantity of hydrogen occluded by copper. I will simply append the list given by him, with the addition of his own name and that of a German chemist, O. Lietzenmayer, who has recently attacked this subject in the *Deut. Chem. Ges. Ber.*, **11**, 306—309.

Weight of copper.	Source.	Hydrogen occluded.
100 grams	Oxide	·0006 (Graham)
,,	Wire	·0003 (Graham)
,,	New wire	·0006 (Thudichum)
,,	Wire re-oxidised and re-reduced	·0001 (Thudichum)
,,	Oxide	·0029 (Melsens)
,,	,,	·0200 (Melsens)
,,	Wire gauze	·0061 (Lietzenmeyer)
,,	Rolled wire	·0074 (Johnson)

The experiments of Graham and Thudichum, whose results I have accordingly bracketed together, were performed on an entirely different principle from the rest, and cannot therefore be fairly compared with those which follow. Even allowing, however, for the fact that the first four numbers were obtained by removing the occluded hydrogen with Sprengel's pump at a red heat and measuring it over mercury, whilst the last four were obtained by weighing it as water after oxidising it at a red heat in a current of dry air, there is still sufficient discrepancy between the results of experiments conducted upon similar principles to demand a careful examination into its cause. This discrepancy I hope to account for satisfactorily by the results of the following experiments; but I will first point out two facts which are

noticeable in the above table: first, the amount of hydrogen found is far greater in the second set of experiments than in the first; and secondly, the second method of experimentation is obviously the one which is best suited for settling the question at issue, viz., how far the occlusion of hydrogen by copper may influence the accuracy of results obtained in organic analysis, inasmuch as the occluded hydrogen is sure to meet with sufficient oxygen, in most analyses at all events, to convert it entirely into water.

The first set of experiments, then, was undertaken with a view to place beyond doubt the answer to the question, whether copper does or does not occlude sufficient hydrogen to introduce a serious error in organic analysis. The experiments were conducted upon the same principle as before, viz., the copper was oxidised at the blowpipe, reduced in hydrogen, allowed to cool in that gas,* and the metal was then re-oxidised in a current of dry air, the water produced being collected in a counterpoised V-tube containing pumice moistened with strong sulphuric acid. Further precautions were, however, taken to avoid the presence of extraneous moisture, atmospheric or otherwise, in the counterpoised drying-tube. For this purpose the air or oxygen in which the charged copper was oxidised was in all cases dried, not only by solid caustic potash and strong sulphuric acid, but also, and finally, by passing through a V-tube containing phosphoric anhydride. Any error due to moisture contained in *corks* was also avoided, the front of each combustion-tube being drawn out and connected with the weighed pumice-tube by india-rubber tubing. In every experiment the dry air or oxygen was drawn through the *cold* apparatus till the pumice-tube had constant weight, after which heat was at once applied to the copper without in any way disturbing the connections.

Occlusion of Hydrogen by Copper in different states.

The first conclusion arrived at was as follows:—When metallic copper is repeatedly oxidised and reduced by hydrogen in the same tube progressively decreasing quantities of hydrogen are occluded till a minimum (apparently constant) quantity is reached. Thus 47·6 grams of rolled copper wire yielded the following weights of water in a series of oxidations in the same tube, each oxidation being of course followed by reduction:—

Experiment	I.....	0·006	gram.
,,	II.....	0·0055	,,
,,	III.....	0·006	,,
,,	IV.....	0·0045	,,
,,	V.....	0·0045	,,

* The hydrogen was displaced from the tube by dry air.

37 grams of rolled wire yielded the following weights of water when treated in precisely the same way:—

Experiment	I.....	0·010	gram.
,,	II.....	0·0103	,,
,,	III.....	0·0085	,,
,,	IV.....	0·004	,,
,,	V.....	0·004	,,

It was conclusively proved in the above experiments that the purity of the *hydrogen* employed for reduction did not in any way influence the result as regards the quantity of that gas occluded by the copper. Hydrogen passed through solution of silver nitrate, and completely dried by P_2O_5, produced results apparently identical with that which had simply passed through one bottle containing strong sulphuric acid. It would appear from the following experiment that the amount of *oxide* on the surface of the copper at the time of its reduction in hydrogen materially influences the subsequent occlusion.

18·8 grams of rolled copper-wire never ignited in air or oxygen, and presenting a clean metallic surface, was reduced in hydrogen at a red heat and cooled in the gas. After intense ignition in dry air for half an hour only 0·0013 gram of water had been collected, whereas the same copper, after being strongly ignited at the blowpipe and again reduced in hydrogen, yielded 0·0045 gram of water.

Again, the same 37 grams of copper which were used in previous experiments and yielded when last oxidised after reduction only 0·004 gram of water, having been strongly ignited in the blowpipe and again reduced, furnished 0·0115 gram of water at a red heat in air.

It appears, then, that the pulverulent metal resulting from reduction of *oxide* on the surface of the copper is the most active agent in occluding hydrogen, and the progressively decreasing amount of gas taken up may readily be accounted for by the *condensation* which this metallic powder undergoes when heated strongly in hydrogen gas, the final result being that much dense metal is produced and less surface is consequently offered for absorption.

These deductions receive further confirmation from the following experiments:—

16·1 grams of pulverulent copper, obtained by reducing 20·2 grams of copper oxide (prepared by igniting carbonate of copper) in hydrogen at a red heat and allowing the reduced metal to cool in that gas, yielded 0·032 gram of water when oxidised in a current of dry air. This is equivalent to ·020 gram of hydrogen for 100 grams of copper.

Even the finely-divided metal resulting from reduced oxide, however, undergoes such condensation by repeated reductions in hydrogen

that its occluding power is finally almost lost. This is clearly proved by these two observations:—

(1.) 18·3 grams of copper, obtained from the same source as that employed in the above experiments, viz., by ignition of cupric carbonate, but which had been frequently oxidised and reduced, was once more oxidised by strong ignition in the blowpipe and then reduced in hydrogen at a red heat and allowed to cool in the gas. Only ·0035 gram of water was obtained on heating the reduced metal to redness in a current of dry pure air.

(2.) 16·6 grams of copper, from the same source and subjected to the same treatment as the above in every way, yielded only 0·009 gram of water in one experiment and 0·0055 gram H_2O in a second experiment, when oxidised in air, after reduction in hydrogen.

But it was noticed that in the above experiments that a potash-bulb placed between the pumice-tube (for absorption of water) and the aspirator underwent an increase in weight each time the copper was ignited in air, and that not only in the case of reduced oxide, but also when rolled copper wire was made use of. The contents of the potash-bulb (which had been filled with pure potash) were found on analysis to consist not of potassic carbonate, but *potassic sulphate;* and as the weight of the bulbs was quite constant when dry air was passed through the apparatus in the cold, this sulphuric acid was accounted for by oxidation of sulphur contained in the copper. A possible source of error, leading to an exaggeration of the weight of hydrogen really occluded by the copper, was here detected, viz., the retention of SO_3-vapour by the sulphuric acid contained in the pumice-tube, leading to an increase in its weight not due to water produced by oxidation of occluded hydrogen.

With a view to determine the *absolute weight* of hydrogen occluded by copper under very favourable circumstances, and at the same time to ascertain if possible how far the error above-mentioned might have affected the accuracy of previous results, the following experiment was executed:—

72·3 grams of copper oxide, intended for organic analysis, was strongly ignited before the blowpipe, reduced in a current of hydrogen in a combustion-tube at as low a temperature as possible, and allowed to cool in the gas. The finely-divided copper thus obtained (after displacement of the hydrogen by dry air) was now heated to redness in dry air, the resulting vapours and gases being drawn by an aspirator through—

(1.) A counterpoise V-tube containing phosphoric anhydride.

(2.) A counterpoise set of bulbs containing pure solution of potash.

(3.) A counterpoise V-tube containing pumice moistened with sulphuric acid.

The P_2O_5-tube increased 0·184 gram. Large drops of water were visible during the early stages of the process. The oxide employed was equivalent to 57·74 grams of metallic copper, so that the weight of hydrogen occluded was in the proportion of 0·035 gram to 100 grams of copper. Inasmuch as a portion of P_2O_5 was converted into a paste by the moisture produced, it is quite possible that some SO_3 may have been retained and added to the weight of water in this experiment, but it is probable that the error thus produced is slight, for the potash-bulb, which was placed beyond the drying tube, underwent an increase of 0·023 gram, which agrees nearly with the results obtained in former experiments. Since the potash-bulb was provided with a small drying tube, the pumice and H_2SO_4-tube beyond underwent no change in weight.

Now as the weight of the above apparatus was unchanged in its various parts by the passage of dry air through it for one hour, there is no source of SO_3 or SO_2 in the form of gas, except the metallic copper in the combustion-tube (which must have been contaminated with sulphur).

The contents of the potash-bulb after the experiment were found to be free from nitrite, *i.e.*, when acidulated with dilute sulphuric acid, the liquid produced no blue colour in a solution of starch and iodide of potassium, but abundance of *sulphate* was found.

It appears from the above results that the sulphur contained in metallic copper undergoes conversion into SO_3 when the metal is oxidised in dry air. Both the copper carbonate and the oxide of copper for organic analysis showed contamination with S by $Ba(NO_3)_2$ add to their solution in HNO_3.

The following experiments, in which *granulated* copper was employed, illustrate the influence of surface upon the weight of hydrogen occluded on the one hand and that of repeated oxidation and reduction in diminishing the occlusive power on the other :—

36·4 grams of granulated copper, after being roasted in air and subsequently reduced in hydrogen, yielded 0·0838 gram of water when oxidised in dry air. This is equivalent to 0·0255 gram of hydrogen to 100 grams of copper.

Again, 46 grams of the same copper similarly treated gave 0·0995 gram of water.

The same copper, after four reductions, occluded hydrogen equivalent to 0·027 gram of water, or only one-third of the original weight.

The above experiments seem to establish beyond all doubt the fact that commercial copper does occlude hydrogen, sometimes in considerable quantities, and apparently always in sufficient quantity to produce a serious error in organic analysis. They also account quite

satisfactorily for the discrepancies observed between the occlusive power assigned by various chemists to the metal.

The following experiments, however, show that physical condition, or extent of *surface* offered by the metal, is not a sufficient explanation of the wide differences observed between the weights of water or hydrogen obtained from equal weights of reduced metal in the experiments I have just described.

It occurred to me that the copper obtained by reduction of precipitated oxide at a very low temperature, as in the experiments of Dr. Wright (*Chem. Soc. Jour.*, p. 13 of this volume), would be in an extremely advantageous form for occluding large quantities of hydrogen. Accordingly I precipitated a boiling solution of pure sulphate of copper with some hot solution of pure caustic potash, and washed the precipitate by decantation with boiling water almost daily for some weeks, till at last, not only were the washings free from sulphuric acid, but some of the oxide, when dissolved in pure nitric acid, gave no precipitate with solution of baric nitrate after standing for 48 hours.

I found that this pure precipitated oxide of copper, after being dried in a tube at 110° in a current of dry air, gave rather more than the calculated quantity of water when reduced in dry hydrogen at 110°. I subsequently discovered that this was due to incomplete drying of the oxide at 110°. The oxide is not *entirely* reduced in pure dry hydrogen at 110°, and either the unreduced oxide or the freshly reduced metal retains some *water* at 110°, which it parts with at a higher temperature, but not a trace of hydrogen is occluded. These facts are established by the following experiments:—

(1.) 3·792 grams of copper obtained by reducing pure precipitated CuO in pure dry hydrogen at 110° was heated to redness in dry hydrogen, a counterpoised V-tube, containing pumice moistened with sulphuric acid having been adjusted. After cooling in the hydrogen the copper had lost 0·025 gram in weight, whilst the pumice-tube had gained 0·030 gram, or more than would be accounted for by oxygen in the copper.

To ascertain whether hydrogen escaped unoxidised when the copper was heated to redness in air—

(2.) Dry air was passed through a tube containing 3·65 grams of Cu reduced at 110° (from same source as above) and then through a tube containing dry CuO, finally through a counterpoised pumice and sulphuric acid tube. The copper oxide was first ignited strongly, then the reduced copper, dry air passing all the time; the pumice-tube increased 0·010 gram in weight.

Hence 3·65 grams Cu evolved 0·01 gram H_2O at red heat in air.

It is clear that the water collected from the copper ignited in dry

air must either be due to retained moisture or to the oxidation of occluded hydrogen, whilst the water obtained from the same copper when ignited in *hydrogen* must be assigned to the same cause, or to the reduction of CuO unacted upon at 110°, but speedily attacked at a red heat in hydrogen gas. Suppose the reduction at 110° to be complete and hydrogen gas to be occluded by the reduced copper, it is evident that the hydrogenised metal will lose weight when heated to redness in hydrogen without any formation of water; or, if it be capable of retaining occluded hydrogen at a red heat, its weight will remain constant, provided that it has retained no *moisture* at 110°. If it has retained moisture, but occluded no hydrogen, the loss it will sustain will be equal to the gain of a drying tube placed in front; whilst, if the reduction at 110° is incomplete and moisture has been retained as well, the gain by such a drying tube will be much in excess of the loss of weight by the copper, and the latter was actually observed in the above experiments. Thus 3·792 grams of copper reduced from precipitated Cu at 110° yielded 0·03 gram of water collected in the drying tube, whilst it lost 0·025 gram in weight. This experiment, then, clearly proves that no hydrogen was occluded by the copper at 110°, for, had the copper retained hydrogen, it would have lost weight either equal to that gained by the drying tube or in excess of that quantity.*

If 3·65 grams lose 0·01 gram H_2O, 3·792 grams would lose ·0104 gram H_2O.

Hence 0·0146 gram out of the 0·025 gram lost by 3·792 grams of Cu reduced at 110°, when heated to redness in dry hydrogen, would be due to oxygen retained by the copper at 110° in hydrogen, whilst 0·0196 gram of the water collected and weighed would be due to the product of combination of that retained oxygen with hydrogen at a red heat; and the theoretical quantity so produced would be 0·0163 gram. It is obvious that had hydrogen been occluded at 110°, which was evolved in hydrogen at a red heat, the loss by the copper in the above experiment would have been in excess of the gain by the pumice-tube, whereas the reverse was actually observed. Hence water, not hydrogen, is evolved in hydrogen at a red heat by copper reduced at 110° in hydrogen.

(3.) It was proved that the same copper, after being subjected to a red heat in hydrogen and cooled in the gas, had not occluded hydrogen even at that temperature; for, when it was oxidised in dry air at a red heat, a pumice-tube placed in front had a perfectly constant weight.

(4.) Even if the pure precipitated oxide of copper be strongly

* The hypothesis that reduced spongy copper may contain occluded hydrogen in presence of unreduced copper oxide is not here discussed, since the existence of such a phenomenon cannot be proved by the method of experimentation employed.

heated in air before being reduced in hydrogen, the spongy metal, whether the reduction be at a high or low temperature, appears to occlude none of the gas.

Thus, then, the most finely divided metal conceivable does not occlude any hydrogen, which clearly proves that some other influence governs the occlusion of hydrogen by copper, besides the mere state of subdivision in which the metal happens to be at the time when it is reduced in the gas.

Remembering the interesting results obtained by Prof. Gladstone and Mr. Tribe (*Chem. Soc. Jour.*, **33**, 308) upon the reducing action of hydrogenised copper on potassium chlorate, &c., I reduced some common copper oxide (intended for organic analysis) in hydrogen in the usual way, washed it with boiling water till the washings gave no precipitate with silver nitrate solution. After boiling this reduced pulverulent metal with some pure potassium chlorate for half an hour abundance of *chloride* was detected in the supernatant liquid. On the contrary, the pulverulent metal, obtained by reduction of precipitated copper oxide at 110° in hydrogen, produced *no chloride* after boiling for one hour with the same potassium chlorate. Thus finely divided copper itself appears to be without action upon a boiling aqueous solution of potassium chlorate, whilst the conclusion that this form of the metal does not occlude hydrogen receives confirmation from the above experiments. Moreover, the reduction of potassic chlorate by hydrogenised commercial copper was proved to be due to its occluded hydrogen, and not to *couple-action* of metallic impurities, by the following experiment:—

Some of the commercial (impure) copper oxide employed in the above experiment was reduced in hydrogen in the usual way. It was then divided into two equal portions, one of which was simply freed from its contained chlorides by washing, whilst the other was first ignited in pure nitrogen, allowed to cool in that gas and then washed with water. The two portions of pulverulent copper thus prepared were now boiled with equal volumes of the same solution of pure potassic chlorate. The supernatant liquors being tested with solution of silver nitrate, that above the hydrogenised copper showed evidence of reduction of its chlorate by the precipitate of silver chloride which it yielded, whilst that which had been boiled over the copper freed from occluded hydrogen by ignition in nitrogen yielded no precipitate with silver nitrate solution.

Behaviour of Hydrogenised Copper in different Gases.

Having now definitely answered the question whether commercial copper recently reduced in hydrogen occludes that gas, my attention

was next directed towards offering some explanation of the vast discrepancy between the results obtained by chemists who heat the charged copper in a current of dry air and those produced by the method of heating to redness in a vacuum and measuring the gas evolved by the Sprengel pump. The explanation which naturally uggested itself was, that the charged copper refuses to part with its occluded hydrogen at a red heat in a vacuum. Accordingly I made some experiments with a view to ascertain whether the hydrogenised copper would retain its occluded gas when heated to redness in a current of gases which have no oxidising action at high temperatures. The first gas tried was *carbonic anhydride*. It soon became manifest, however, that this gas was quite unsuited for the purpose; for in several experiments quite ponderable quantities of water were evolved by recently reduced copper when heated to redness in a current of dry CO_2. Thus, 27 grams of copper yielded in one experiment 0·009 gram H_2O; in another, 0·013 gram; in another, 0·011 gram. The only possible explanation of these results being that the hydrogen was oxidised by the CO_2 at the temperature of the Hofmann's furnace, the following experiments were undertaken, in order to ascertain whether this reaction was dependent upon the presence of a metallic surface, or whether it would take place when the two gases were simply subjected to a high temperature in presence of some indifferent body.

By means of a T-shaped tube, a stream of mixed carbonic anhydride and hydrogen gases was passed through the following purifying apparatus:—(1.) A solution of sodic bicarbonate. (2.) A solution of silver nitrate. (3.) Two pumice-tubes containing strong sulphuric acid, and (4.) A U-tube containing phosphoric anhydride. The purified gases were next conducted through a combustion-tube filled with fragments of broken porcelain, and finally through a tube containing pumice and sulphuric acid. The weight of this last tube was taken when filled with hydrogen; and this gas was always passed in the cold till the counterpoised tube had a constant weight after one hour before each experiment. The apparatus being thus proved to be in thorough working order, the mixed gases (CO_2 and H) were conducted through the combustion-tube together, the temperature being kept at red heat for a given time, after which the supply of carbonic anhydride was stopped and the dry hydrogen passed alone for some time; the pumice-tube was then again weighed full of hydrogen, the increase giving of course the weight of water produced during the application of heat:—

In Experiment I,	0·047 gram of H_2O	was produced in	$1\frac{3}{4}$	hours.
,, II,	0·030	,,	$1\frac{1}{2}$	,,
,, III,	0·060	,,	,,	,,

These results were considered to prove satisfactorily that hydrogen is slowly oxidised by CO_3 at the highest temperatures of the combustion (Hofmann's) furnace. The gases were not *drawn* through by an aspirator, but were *driven* through from behind by the pressure produced in gas generators.*

The next gas employed was carbonic oxide. Even when the utmost precautions were taken to purify this gas, small quantities of water appeared to be produced during ignition of the hydrogenised copper therein, and this even when an alkaline pyrogallate was employed to remove traces of oxygen. Thus 46 grams of granulated copper when ignited in the dry pure gas yielded 0·008 gram H_2O, or at least there was so much increase in the weight of a counterpoised pumice and H_2SO_4-tube, whose weight had been constant for one hour whilst the CO was passed in the cold. The same copper, however, after being cooled in the CO, was ignited strongly in a current of pure dry air and yielded only 0·001 gram of water; whilst, after being again reduced in dry hydrogen, cooled in that gas and ignited in dry air only, it yielded 0·027 gram of water. Hence the copper cannot retain its occluded hydrogen in a current of carbonic oxide gas; for the occlusive power of the copper in the above experiments was proved to be equivalent to 0·027 gram of water, whilst only 0·009 gram H_2O was produced from it by alternate ignition in CO and dry air; therefore two-thirds of its occluded hydrogen must have escaped unoxidised during the ignition in carbonic oxide.

The same result was obtained by employing *nitrogen* carefully purified. No water could be obtained by igniting in dry air copper which had been heated to redness in pure nitrogen, and allowed to cool in that gas, after being previously charged with hydrogen.

It appears, then, that hydrogenised copper cannot retain its occluded gas when ignited in a current of carbonic oxide or nitrogen.

I now repeated the experiments of Graham and Thudichum, and obtained precisely similar results. Mere traces of hydrogen were collected (in most experiments) by the Sprengel pump.

The retention of hydrogen by freshly reduced pulverulent copper heated to redness in a vacuum is proved by the following experiment:—

35·3 grams of powdered oxide which had been made into a paste with nitric acid, *fused* and then powdered in a mortar, were reduced in pure dry hydrogen and allowed to cool in the same gas. The tube containing the freshly reduced metal was now exhausted by Sprengel's pump, and its temperature raised to the full red heat of a Hofmann's

* Reduction of CO_2 by H at a red heat: vide *Watts' Dict.*, article "Marsh-gas;" item Lowthian Bell, "Chemical Phenomena of Iron-Smelting," pp. 122–126.

Reduction of CO by H at a red heat: *vide* I. L. Bell, *loc. cit.*, p. 131.

furnace. The tube having remained vacuous and collapsed for one hour, no measurable gas was collected. The copper, having cooled in the vacuous tube, was now introduced into a dry combustion-tube and ignited in carefully dried air, when 0·062 gram of water was collected and weighed.

In a similarly conducted experiment, 23·47 grams of copper oxide yielded 0·037 gram of water after reduction in hydrogen, ignition in a vacuum, and final oxidation in dry air.

The fact that hydrogenised copper parts with its occluded hydrogen when ignited in a current of nitrogen gas, was made use of to afford corroborative evidence that the *hydrogen* and not simply *water* is occluded by copper reduced from its oxide by that gas.

Samples of commercial copper oxide were reduced in hydrogen as in previous experiments at different temperatures, and afterwards ignited in dry pure nitrogen gas, carefully freed from oxygen, the gases issuing from the combustion-tube being conducted through (1) a counterpoised sulphuric acid tube, (2) a tube containing ignited oxide of copper, and (3) a second counterpoised sulphuric acid apparatus. It was found that when the reduction of the metal had been effected at temperatures below 700°, water was always evolved, and caused an appreciable increase in the weight of the first drying bulb; whilst the second drying tube also showed evidences of hydrogen occluded *as such* in the copper, evolved in the nitrogen and oxidised by the ignited copper oxide. On the other hand, when the temperature of reduction was increased to a red heat, and when the hydrogen was passed at that temperature *till no ponderable water was evolved*, the first drying tube retained a constant weight during the ignition of the copper in nitrogen, whilst the second tube appreciably increased in weight, visible drops of moisture being often observed in front of the red-hot copper-oxide tube.

A very probable explanation of the discrepancy between results obtained by Drs. Thudichum and Hake and my own, has been offered by my friend Dr. C. R. A. Wright (to whom I am also indebted for several other valuable suggestions), viz., that some of the occluded hydrogen may be oxidised by unreduced *suboxide of copper*, retained in the deeper strata of the metal, such oxidised hydrogen, of course, escaping detection by the process of Sprengelising the hydrogenised copper. And this explanation is rendered additionally probable by the observation that copper reduced at *low temperatures* yields *water* as well as hydrogen when ignited in a stream of pure nitrogen; for it is at least as plausible an explanation of this fact to assert that some suboxide of copper which escaped reduction at that low temperature, became reduced by a portion of the occluded hydrogen evolved at the higher temperature of the ignition in nitrogen with production of

University of Michigan

water, as to say that this water had been occluded in the metal as such.

The practical result, however, arrived at by the above experiments is sufficiently obvious, viz., that it is unsafe to employ copper freshly reduced in hydrogen for the reduction of oxides of nitrogen in organic analysis, unless the metal be previously ignited in nitrogen gas.

XXXI.—*On Plumbic Tetrethide.*

By E. Frankland, F.R.S., and Awbrey Lawrance, Esq.

In the year 1859, Buckton (*Phil. Trans.*, **149**, 431) described the preparation of plumbic tetrethide, established its constitution, and announced its chief properties; but no further study of the reactions of this body having since been made, we beg to submit to the Society the following observations upon its behaviour in contact with various gaseous reagents.

After exposure to an atmosphere of each of the following gases for a period varying from eight to eleven days, we found that no action took place, and that there was no perceptible diminution in the volume of the gas:—Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen. On the other hand, sulphurous anhydride was rapidly absorbed, converting the liquid plumbic tetrethide into a white amorphous solid.

Action of Sulphurous Anhydride on Plumbic Tetrethide.

For the preparation of the plumbic tetrethide used in these experiments we employed a modification of Buckton's method. Dry plumbic chloride was added to zinc ethyl so long as any reaction took place. A large quantity of metallic lead in a spongy condition was deposited without any evolution of gas, whence we infer that the dyad compound ($PbEt_2$) is first formed and then decomposed according to the following equations:—

$$PbCl_2 + 2ZnEt_2 = PbEt_2 + 2ZnEtCl.$$
$$2PbEt_2 = Pb + PbEt_4.$$

It has been shown by one of us (*Phil. Trans.*, **142**, 417) that stannous ethide is similarly decomposed, though less readily into stannic ethide and metallic tin:—

$$2SnEt_2 = Sn + SnEt_4.$$

and we have recently availed ourselves of this transformation for the preparation of large quantities of stannic ethide (*Jour. Chem. Soc.*, 1879, p. 130).

The initial process in the preparation of plumbic tetrethide is best conducted in a stout glass bottle in which the mixture can be well stirred with a glass rod, and the plumbic chloride should be added until it no longer changes colour. Instead of separating the crude plumbic tetrethide by water, and distilling it *in vacuo* to avoid decomposition as recommended by Buckton, we found the following plan simpler and quite satisfactory.

The product of the reaction was slowly mixed with a large volume of water in a capacious flask or retort, which was then placed in an oil bath and its contents distilled in a current of steam so long as any heavy oily drops passed over. The distillate consisted of water and a heavy layer of plumbic tetrethide which, when separated, was ready for the following reaction. Before adopting this process it was ascertained that plumbic tetrethide suffers no decomposition by distillation with water.

Several ounces of plumbic tetrethide were placed in a Winchester quart bottle filled with dry sulphurous anhydride, which was afterwards supplied as often as necessary. The colourless liquid first changed to a yellowish-green turbid and thick oil, and finally, after forty-eight hours, became a white amorphous solid, refusing to absorb more of the gas. Preliminary experiments showed that this amorphous mass was, to a large extent, soluble in water, the insoluble residue consisting chiefly of plumbic sulphite or sulphate; and that, either dry or dissolved in water, it gave a splendidly crystalline sublimate when heated to 100°. Guided by these observations, the white amorphous product was put into a beaker, to the mouth of which a second beaker was luted with gummed paper, and a steam heat was then applied to the first beaker for several hours. In this way a considerable bulk of crystals sublimed into the second beaker, although their weight was but small. These crystals possessed the properties of diethyl sulphone (SO_2Et_2), but they were contaminated with a volatile lead compound, which left a residue of plumbic oxide amounting to about 5 per cent. of their weight when they were burnt in a stream of air and oxygen. As this residue was not materially diminished by recrystallisation from an aqueous solution, the crystals were dissolved in hot and strong nitric acid, some red fumes were evolved, and on evaporation to dryness the residue suddenly solidified to a crystalline mass. This mass was treated with alcohol in which nearly the whole of it dissolved, the solution was filtered and evaporated to crystallisation, the crystals being afterwards redissolved in water and recrystallised. On combustion they now left only 1·5 per cent. of residue.

Submitted to analysis, the purified crystals gave the following results:—

I. 0·1464 gram burnt with cupric oxide in a stream of air and oxygen, gave 0·2120 gram of carbonic anhydride and 0·1114 gram of water.

II. 0·1158 gram, burnt with a mixture of potassic chlorate and sodic carbonate, gave 0·2250 gram of baric sulphate.

These numbers agree closely with those calculated from the formula of diethyl sulphone, as shown by the following comparison:—

	Calculated.		Found. I.	Found. II.
C_4	48	39·35	39·49	—
H_{10}	10	8·19	8·44	—
S	32	26·23	—	26·68
O_2	32	26·23	—	—
	122	100·00		

The identity of this body with diethyl sulphone is confirmed by a comparison of their chief properties. They are both unacted upon by strong nitric acid, and both melt at 70° C., and suddenly solidify at 55°.

The substance remaining after the separation of diethyl sulphone was dissolved in water and filtered from an insoluble residue, which consisted chiefly of plumbic sulphate. The filtrate, which obviously contained a lead salt, was divided into two parts, one being devoted to treatment with baric hydrate, and the other to the action of sulphuretted hydrogen with a view to the separation of the free acid.

To the first portion an excess of baric hydrate was added, and the copious precipitate of plumbic hydrate separated by filtration. The strongly alkaline filtrate was then distilled in order to separate, if present, any volatile organo-lead base; but the distillate was neutral. Carbonic anhydride was then passed through the residue in the retort to remove excess of baryta, and the liquid was boiled and filtered. The filtrate was next treated with sulphuretted hydrogen to decompose the last traces of lead compound, the black precipitate filtered off, and the solution boiled with baric carbonate and filtered. The filtrate was evaporated to its crystallising point, and a crop of rhomboidal crystals obtained which, after drying at 100°, gave the following results on analysis, and these, taken in connection with the reaction giving rise to this compound, leave no doubt that it is the barium salt of ethyl sulphinic acid (**S**OEtHo) containing one molecule of water of crystallisation, as is seen from the following comparison:—

I. 0·1421 gram, burnt with cupric oxide in a stream of oxygen, gave 0·0474 gram of water and 0·0714 gram of carbonic anhydride.

II. 0·1364 gram, burnt with cupric oxide in a stream of oxygen, gave 0·0451 gram of water and 0·0689 gram of carbonic anhydride.

III. 0·3028 gram, ignited with concentrated sulphuric acid, gave 0·2028 gram of baric sulphate.

IV. 0·2620 gram, burnt with potassic chlorate and sodic carbonate, gave 0·3480 gram of baric sulphate.

Calculated into percentages, these results give numbers agreeing with the formula $(SOEt)_2Bao'',OH_2$, or $C_4H_{12}BaS_2O_5$:—

	Calculated.		Found. I.	II.	III.	IV.
C_4	48	14·08	13·70	13·77	—	—
H_{12} ..	12	3·52	3·70	3·67	—	—
S_2	64	18·77	—	—	—	18·24
Ba	137	40·17	—	—	39·38	—
O_5	80	23·46	—	—	—	—
	341	100·00				

The second portion of the filtrate already mentioned was treated with excess of sulphuretted hydrogen in order to separate free ethylsulphinic acid. A black precipitate and a small quantity of a yellowish oil of a very disagreeable odour were obtained, the solution was filtered, and the filtrate boiled with baric carbonate after the oil had been removed by agitation with ether.

An attempt was made to prepare the silver salt of this acid, but the compound underwent decomposition even in the dark.

The barium salt after purification was submitted to analysis with the following results:—

I. 0·1844 gram of the dried substance ignited with concentrated sulphuric acid, gave 0·1207 gram of baric sulphate.

II. 0·1166 gram, burnt with cupric oxide in a stream of oxygen, gave 0·0357 gram of water and 0·0588 gram of carbonic anhydride.

III. 0·2830 gram burnt with potassic chlorate and sodic carbonate, gave 0·3781 gram of baric sulphate.

These results calculated into percentages give numbers agreeing fairly well with those just given for baric ethyl sulphinate, viz., carbon, 13·75; hydrogen, 3·40; barium, 38·49; sulphur, 18·35.

In another experiment this reaction was carried on in an atmosphere of carbonic anhydride with exactly the same results, as the following analyses of the lead salt show:—

$$[(SOEt)_2Pbo'' = C_4H_{10}PbS_2O_4].$$

I. 0·1687 gram, burnt with cupric oxide in a stream of air and oxygen, gave 0·0738 gram of carbonic anhydride and 0·0413 gram of water.

II. 0·1550 gram, burnt as before, gave 0·0680 gram of carbonic anhydride and 0·0420 gram of water.

III. 0·1617 gram, burnt with a mixture of sodic carbonate and potassic chlorate, gave 0·1817 gram of baric sulphate.

IV. 0·2243 gram gave, after ignition with sulphuric acid, 0·1705 gram of plumbic sulphate.

V. 0·2496 gram, similarly treated, gave 0·1889 gram plumbic sulphate.

	Calculated.		Found. I.	II.	III.	IV.	V.	Mean.
C_4 ..	48	12·21	11·93	11·96	—	—	—	11·95
H_{10} ..	10	2·54	2·72	3·01	—	—	—	2·86
S_2 ..	64	16·28	—	—	15·43	—	—	15·43
Pb ..	207	52·67	—	—	—	51·88	51·70	51·79
O_4 ..	64	16·30	—	—	—	—	—	17·97
	393	100·00						

The formation of diethyl sulphone (sulphuric diethoxide) and plumbic ethyl sulphinate is explained by the following equation:—

$$\underset{\text{Plumbic tetrethide.}}{PbEt_4} + 3SO_2 = \underset{\text{Diethyl sulphone.}}{SO_2Et_2} + \underset{\text{Plumbic ethyl sulphinate.}}{\begin{matrix}SOEt\\SOEt\end{matrix}Pbo''}.$$

Ethylsulphinic acid was discovered by Hobson (*Jour. Chem. Soc.*, **10**, 55), but its formula was first established by Wischin (*Ann. Chem. Pharm.*, **139**, 364). This acid may be considered as derived from sulphurous acid by the substitution of a semi-molecule of ethyl for one of hydroxyl, thus:—

$SOHo_2$	$SOEtHo$
Sulphurous acid.	Ethylsulphinic acid.

It is also equally true that ethylsulphinic acid is propionic acid, in which one atom of tetrad-sulphur has been substituted for one of carbon, thus:—

$\left\{\begin{matrix}C_2H_5\\COHo\end{matrix}\right.$	$\left\{\begin{matrix}C_2H_5\\SOHo\end{matrix}\right.$
Propionic acid.	Ethylsulphinic acid.

The following is a summary of the results described in the foregoing pages:—

1. Plumbic tetrethide in quantity may be most conveniently obtained by distilling with water the product of the action of zinc-ethyl upon plumbic chloride.

2. Prolonged exposure at ordinary temperatures to the following gases produces no chemical change in plumbic tetrethide:—

Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen.

3. Plumbic tetrethide rapidly absorbs sulphurous anhydride, and is transformed into a white solid which is composed of diethyl sulphone (sulphuric diethoxide, SO_2Et_2) and plumbic ethyl sulphinate,

$$\left(\begin{matrix}SOEt\\SOEt\end{matrix}Pbo''\right).$$

4. No volatile organo-metallic base is formed in this reaction, like that which we have shown to be produced in the corresponding operation with stannic ethide (*Jour. Chem. Soc.*, 1879, 130). In the presence of sulphurous anhydride plumbic tetrethide is at once deprived of the whole of its ethyl, whereas stannic ethide retains three-fourths of it.

XXXII.—*On the Decomposition of Water by Certain Metalloids.*

By C. F. Cross and A. Higgin.

Sulphur.—The statements of chemists with respect to the action of sulphur on water are conflicting. According to Mulder (*Jahresber.*, 1858, 84) the vapours of water and sulphur (at high temperatures) react to form pentathionic acid; Meyer, on the other hand (*Compt. rend.*, **74**, 195), states that thiosulphuric acid is formed. Girard (*Compt. rend.*, **61**) found that on boiling pure sulphur with water, a large quantity of hydrogen sulphide was evolved, but his observation is questioned by Gélis (*Compt. rend.*, **56**, 1004), who ascribes the evolution of hydrogen sulphide, which is, he admits, sometimes observed under these conditions, to the presence of impurities in the sulphur.

We have investigated the question by methods similar to and different from those adopted by the above-named observers, the results of which we proceed to detail.

Our first observations were made with lead acetate upon the steam from water, holding sulphur (flowers) in suspension and kept boiling under ordinary conditions in a glass flask; the lead salt was continuously decomposed with formation of sulphide. A tube, bent twice at right angles, was then fitted to the flask, and the steam passed thereby into a solution of lead acetate. Traces only of sulphide were

precipitated, but we found that sulphur was present in some quantity; this apparent distillation of sulphur was unaffected by causing the steam to pass through cotton wool. On raising the boiling point of the water to 101·5°, by the addition of pure sodium sulphate, the quantity of lead sulphide precipitated in an experiment of $3\frac{1}{2}$ hours' duration, was ·0037 gram. In a second experiment, under the same conditions, ·0023 gram of the sulphide was precipitated, whereas the sulphur separated amounted to ·020 gram. In a third, water only was placed in the condensing flask; this rapidly became milky with suspended sulphur, ·0093 gram being present at the end of two hours. On substituting a retort and condenser, the formation and deposition of sulphur could be easily watched in the tubulus, on the sides of which it was curiously aggregated into stellate masses. After distilling 900 c.c. from 5 grams of sulphur, a fourth distillate of 300 c.c. was boiled down with nitric acid and the sulphur present, estimated as $BaSO_4$, was found to amount to ·0194 gram. Observations on a further 300 c.c. satisfied us that the phenomenon was uniform and continuous. In all cases the distillate contained a certain quantity of hydrogen sulphide, of which the odour was very perceptible; this was estimated (by iodine) in 100 c.c. as ·0017 gram. No trace of oxyacids could be detected. The water which remained in the retort, filtered from the sulphur, yielded with barium chloride a precipitate of sulphate, representing ·0077 gram sulphur; the sulphur which has thus undergone oxidation is approximately equivalent to that escaping as hydrogen sulphide, supposing the decomposition to occur according to the equation,

$$2H_2O + S_3 = 2H_2S + SO_2,$$

and the sulphurous acid to be oxidised by atmospheric oxygen. The probability of the latter supposition was increased by the experiment of conducting the distillation in an atmosphere of carbonic anhydride, in which case no trace of oxyacid could be detected in the residual water. The former is supported by the observation that when the condenser was placed in an upright position, no traces of hydrogen sulphide escaped during a period of six hours' heating, whereas sulphur was continuously separated and carried back into the flask. Further, on extinguishing the flame and pouring a solution of lead acetate down the condenser, the lower portion, together with the flask, was instantly blackened by a considerable precipitation of lead sulphide, which is, we think, referable to hydrogen sulphide rather than to a decomposition by sulphur vapour—the alternative explanation.

While the reversal of the above decomposition, which would be determined by a change in the physical condition of the products from that which we may suppose to cause their dissociation, affords an explanation of the apparent distillation of sulphur, the view which we

have advanced rests rather upon the indirect evidence than on any actual proof afforded by our experiments. We attempted to demonstrate the presence of sulphurous anhydride, by adapting to the flask a specially constructed diffusion apparatus, but the steam which accompanies the products proved an insurmountable obstacle to their separation by this method.* We therefore reverted to indirect experiment, and obtained the following additional results. Sulphur was boiled with aqueous lead acetate in an open flask; after 14 hours' boiling the precipitate (lead sulphide and sulphate) was analysed and found to contain for every 100 c.c.:

		Ratio.
S as PbS	·0198 gram	1 to
S as $PbSO_4$	·0152 „	··76

Sulphur was then sealed up in glass tubes with aqueous lead acetate and heated to 150—160° for 6—8 hours. In the first instance sulphur was taken in excess, and the whole of the lead was precipitated from solution as sulphide. The lead salt was then taken in excess; the resulting precipitates were mixtures of sulphide and sulphate, of the following composition respectively (the quantities are calculated for 100 c.c.).

	Gram.	Ratio.	Gram.	Ratio.	Gram.	Ratio.
S as sulphide	·0975	1 to	·1464	1 to	0792	1 to
S as sulphate	·0678	·69	·1098	·75	·0420	·53
Total S in combination	·1653		·2562		·1212	

(The totals thus observed agreed closely with the numbers calculated from the weights of unaltered sulphur obtained.) These results afford further proof that sulphur in decomposing water unites both with its oxygen and hydrogen; the discrepancy between the ratios observed and that corresponding with the hypothetical equation, may be referred to atmospheric oxidation, the amount of oxygen present in our tubes being, as we found by calculation, sufficient for this effect. At the same time this primary decomposition is independent of atmospheric oxygen, as the following experiment clearly shows: Lead acetate solution which had been previously boiled and allowed to cool out of contact with the air, was placed in a tube together with sulphur; the tube was then narrowed, the residual air expelled by a rapid stream of carbonic anhydride, during the passage of which the operation of

* On adding alkaline permanganate to the milky distillate (p. 250), a bright green colour was instantly developed. The thiosulphuric acid, whose presence is thus indicated, may be regarded as formed by the action of SO_2 on S (Flückiger). This seems to us the more probable explanation of Meyer's observation (p. 249).

sealing was continued. In this tube the formation of sulphide was observed to occur at a temperature as low as 95°.

It was now necessary to examine the ground upon which Gélis denies the decomposition of water by sulphur. The evolution of hydrogen sulphide, which he admits is often observed on boiling sulphur with water, he ascribes to the presence of impurities in the sulphur, on the following grounds: (1.) That it does not occur in the case of sulphur which has been treated with potassium permanganate or iodine, and washed; and (2.) on heating sulphur with water to 150—190° in sealed glass tubes, in three out of four experiments, no hydrogen sulphide was perceived on opening the tubes.

We have repeated these observations, but with different results. A portion of the sulphur used in our experiments was allowed to remain for some time in contact with a strong solution of permanganate. Manganic oxide was deposited upon the sulphur and removed by boiling with hydrochloric acid, the sulphur undergoing further oxidation by the chlorine thus liberated. After thorough washing it was boiled with water, which it decomposed as before with liberation of hydrogen sulphide. We also observed that, on boiling sulphur with permanganate solution, it appears to distil precisely as when water alone was used (we found by direct experiments on hydrogen sulphide and sulphurous oxide that either gas, when passed into boiling permanganate, escapes to a large extent unoxidised). With respect to the second point, the absence of hydrogen sulphide in the experiments cited, it is scarcely necessary to say that it in no way proves that which it assumes to do; on the contrary that a similar observation is the basis of our hypothesis. We must, therefore, regard Gélis' statements as unfounded. Flückiger has stated that all preparations of sulphur contain traces of thiosulphuric acid; we could not detect such in that employed by us, and the experiments just detailed prove that our observations are not subject to this source of error. Lastly the alkaline constituents of the glass vessels in which our solutions were boiled appear to be without influence; for in most cases an acid reaction was obtained, and the evolution of hydrogen sulphide occurred when dilute sulphuric acid was substituted for water.

We next examined the sulphur in the retort and in the distillate for solubility in carbon disulphide. In its original state (flowers) it contained 20·2 per cent. of the insoluble variety; after boiling with water it was found to be wholly soluble, whereas on the other hand, that which was present in the distillate was white, and insoluble in carbon disulphide, and probably therefore a product of decomposition.

A less direct but similar case of decomposition of water by sulphur takes place on heating them in presence of iodine. In one experiment 1·27 grams iodine was treated with 25 c.c. of water, and excess of sul-

phur to 160°; the solution became colourless at the end of ten hours. The iodine existed in solution entirely as hydriodic acid, the sulphur as sulphuric acid. This reaction appears to be the reverse of the decomposition of aqueous hydriodic acid by sulphur (*Watts's Dictionary*, 1, Suppl., 739). Certain points of *à priori* evidence which favour our hypothesis remain to be mentioned. Thus carbon disulphide is resolved by the action of water at high temperatures into carbonic acid and hydrogen sulphide (Schlagdenhauffen, *J. Pharm.*, [3], **29**, 401). It was interesting to us, in its bearing upon our previous experiments, to investigate the influence of the presence of lead acetate upon this reaction. In one experiment, when this salt was in excess ·509 gram of the precipitate was found to contain ·3305 gram PbS and ·168 gram $PbCO_3$, quantities which closely satisfy the equation: $2H_2O + CS_2 = 2H_2S + CO_2$. In a second experiment, the disulphide being in excess, the contents of the tube were under considerable pressure, and the precipitate contained 94 p.c. of sulphide, 1·5 p.c. of carbonate, the residual 4·5 p.c. consisting probably of free sulphur, the formation of which is known to attend the decomposition of the disulphide by water alone. It appears, therefore, that the reaction is simplified by the presence of a body capable of uniting with the products. It is also to be remembered that sulphur decomposes both the aromatic hydrocarbons and the paraffins with formation of hydrogen sulphide and liberation of carbon.* We therefore conclude that sulphur decomposes water, and infer on the evidence indirect and *à priori* which we have discussed that it does so, by uniting with both its hydrogen and oxygen. At the same we are of opinion that the observed distillation of sulphur is chiefly referable, not to the reunion of the products of this decomposition—for we find that sulphur also accumulates in the distillate when a current of hydrogen sulphide or of sulphurous anhydride is continuously passed through the water (boiling in presence of sulphur)—but rather to the fact that sulphur is vaporised by steam, in same way as paraffin and other bodies of high boiling point, and that a portion of the vapour thus formed reacts with the vapour of water at the temperature of 100° (and even below 100°), forming a hydrogen and an oxygen compound.

Selenium and *tellurium* we found to exert an inappreciable action upon water at a temperature of 160°.

Phosphorus.—The amorphous variety does not appear to decompose water when boiled with it in an open flask. A slight reaction occurs at higher temperatures.† Thus on heating a small quantity with 25 c.c. of water to 160° for about 32 hours, the quantity of phosphorus in

* In repeating these observations we obtained from toluene graphitic scales, while the carbon obtained from the paraffins resembled lamp-black.

† In presence of air.

solution amounted to ·0096 gram, of which ·0055 gram had been fully oxidised to phosphoric acid. On replacing the water by a solution of lead acetate, the reaction was much increased, and a bulky precipitate, consisting of metallic lead, phosphate, and an unstable phosphide, was formed. With copper sulphate we obtained a similar result: a considerable quantity of metallic copper was deposited, largely in the form of long needles, mixed with a phosphide which will presently be described, and sulphide, the solution containing sulphuric and phosphoric acids. (The reduction of the sulphuric acid is worthy of remark.)

The reduction of cupric chloride by phosphorus is more striking. On heating the aqueous solution of this salt also with the amorphous variety at 160° for eight hours, it underwent complete reduction to cuprous chloride, which crystallised on cooling in large foliated plates. On again heating at 160° for eight hours, the chloride was entirely decomposed, yielding a phosphide of definite composition, which was obtained as a semi-metallic powder of sp. gr. 4·874. Two analyses of this body gave the following results:—

(*a*.) ·388 gram gave ·3358 gram CuO and ·443 gram $Mg_2P_2O_7$.
* (*b*.) ·388 „ ·460 „ „ ·611 „ „

	(*a*.)	(*b*.)	Calc. Cu_nP_n.
Copper	68·98	68·36	67·2
Phosphorus ..	31·66	31·64	32·8
	100·64	100·00	100·0

This phosphide is insoluble in hydrochloric acid; it decomposes potassium cyanide in the cold, with evolution of hydrogen phosphide, and corresponds therefore with that described by Miller (*Elements*, **2**, 701) as resulting from the action of phosphorus, presumably vitreous, on a boiling solution of copper sulphate, and formulated as Cu_2P_2 under a note of interrogation. We have, however, been quite unable to prepare this body by the method there stated, the precipitate so obtained containing also metallic copper and an oxy-salt in varying proportions. Thus in four experiments under similar conditions the precipitates obtained were found to contain the following percentages of copper respectively, 31·66, 32·75, 34·68, and 36·08. In the first of these the sum of the percentages of copper and phosphorus was only 89·25. Further these precipitates on exposure to the air underwent oxidation accompanied by deliquescence, and on subsequent treatment with water yielded a green solution, which on evaporation deposited

* Ratio Cu : P only determined. The excess of copper over the calculated percentage is due to the unavoidable formation of a small quantity of the metal.

metallic copper as a bright red powder, whereas the phosphide described by us is perfectly stable in the air.

It will be seen from these observations that amorphous phosphorus decomposes water freely at high temperatures in presence of metallic salts capable of forming insoluble compounds with the products; the reaction appears to be similar to that which occurs with the alkalis, the precipitation of phosphide indicating the previous formation of hydrogen phosphide, and the separation of metal the formation of hypophosphorous acid as a stage in the reaction.

Vitreous Phosphorus.—The question of the decomposition of water by this variety was investigated by observations similar to those detailed in the case of sulphur. When boiled with water under ordinary conditions in a flask attached to a condenser, phosphorus accumulates in the distillate; phosphoric and phosphorous acids are formed and dissolved by the boiling water, and the distillate gives the reactions of hydrogen phosphide. If, on the other hand, the distillation is conducted in an atmosphere of carbonic anhydride, no traces of oxy-acids are formed, whereas the distillation of phosphorus is unaffected. We conclude, therefore, that phosphorus, like sulphur, is vaporised by steam, but does *not* decompose boiling water, except in presence of oxygen. This accords with a recent observation of J. Corne (*J. Pharm. Chim.* [4], **28**, 386), that moist phosphorus reduces iodic acid and the iodates at ordinary temperatures in presence of air, but is without action if oxygen be excluded.

On sealing a tube containing lead acetate solution and phosphorus, after expelling the air with a current of carbonic anhydride, and placing it in hot water at 80—90°, we observed that reduction took place; a black phosphide was formed, which when thrown on to a filter underwent rapid oxidation to phosphate. Phosphorus appears, therefore, to reduce metallic solutions, *i.e.*, to decompose water, in presence of metallic salts, even when oxygen is excluded.

Halogens.—Bromine was heated with many times its volume of water for eight days at 160°; no pressure was observed on opening the tubes, and the whole result of the experiment was the formation of a small quantity of alkaline salt. Iodine was found to be similarly dissolved in small quantity as alkaline iodide and iodate. On replacing the water by a solution of lead acetate, the addition of bromine caused the precipitation of a brown mass resembling lead dioxide. This compound, after washing and drying, was found to contain 13 per cent. bromine (12·92 and 13·17 in two analyses) and 73·3 per cent. lead. By washing with boiling water for some hours the percentage of bromine was reduced to 12·1. After then treating with hot dilute acetic acid and washing with water, a residue of the pure dioxide was obtained (Pb = 86·3 per cent., calc. 86·6). On heating the original

precipitate with water at 160° (containing also acetic acid) we obtained, on cooling, a crystalline mass of lead bromide mixed with a small quantity of carbonate (Pb = 57·56 per cent., calc. PbBr = 56·4). We confirmed the latter observation by a direct experiment on the dioxide, which we find is dissolved by dilute acetic acid at high temperatures, a small quantity of the latter being simultaneously oxidised to carbonic acid. It is evident, therefore, that bromine decomposes water in presence of lead acetate, with formation of a hydracid (*i.e.*, lead bromide) and liberation of oxygen (*i.e.*, formation of lead dioxide).

Since writing the above we have made the following observations: Absolute alcohol was distilled from sulphur (flowers); the distillate contained no trace of sulphur. Aqueous alcohol was then substituted, and the "distillation" of sulphur found to begin at 92°. The bearings of these points upon the discussion of p. 253 are evident.

ANNIVERSARY MEETING,

March 31st, 1879.

Dr. GLADSTONE, F.R.S., President, in the Chair.

The following report was read by the President:—

In the bye-laws of our Society, as revised a twelvemonth ago, one purpose of the Annual General Meeting is stated to be "for receiving the Report of the President on the State of the Society." During the years that have elapsed since the first anniversary in 1842, the report has been that of the President and Council; yet under the somewhat altered circumstances, I do not feel that I can do better than follow again the good example of my predecessors in this chair, and tell the tale of our annual progress in much the same form as heretofore. I have neither the right nor the power to divest myself of official responsibility, and I certainly have not the desire to express any opinion which would not be concurred in by my colleagues of the Council.

The state of the Society affords much ground for congratulation, as we have passed through a year of quiet prosperity. Considerable additions have been made to our roll of fellowship, while remarkably few have passed away from us by death. There has been an unusual number of scientific papers communicated to us; our Journal has grown in circulation and usefulness; our Library has been much improved; and our funds are in a healthy condition.

Our history has been of that happy character which leaves little to record, and nothing to explain. In my last year's address I mentioned bye-laws that were to be amended; arrangements that were being made for improving the management and publication of the Journal; and the hopeful commencement of the Research Fund. What was then a matter of promise has now been fully realised.

An analysis of the numerical gains and losses of the Society gives the following results:—

Number of Fellows last anniversary		938
Since elected and paid admission fees		61
		999
Removed on account of arrears	8	
Withdrawn	5	
Deceased	5	
	—	18
Present number of Fellows		981

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Number of Foreign Members last anniversary	35
Deceased	1
Present number of Foreign Members	34
Associate	1

The increase of Members has been doubtless greater than it otherwise would have been on account of many chemists having previously deferred their candidature; while on the other hand, through the difficulty of obtaining the necessary quorum, there are 28 names awaiting election at the present moment.

The Treasurer's report, as usual, is given separately, and shows an increase of receipts over expenditure to the extent of £1,964 9*s*. 5*d*. This, however, is mainly due to another legacy of £1,000. It was bequeathed to us, along with similar sums to three other learned Societies, by Mr. Sydney Ellis, the youngest son of Mr. Edward S. Ellis, of Leicester. He was not a Fellow of our Society, but was very fond of scientific pursuits; life was opening before him full of promise, when unfortunately one day last October, while alone in his laboratory, and as is supposed making some blue colours with cyanides, he accidentally inhaled some gas which proved suddenly fatal.

The Papers read before the Society have been as follows:—

I. "On Terpin and Terpinol:" by W. A. Tilden.

II. "The Poisonous Principle of *Urechites Suberecta*:" by J. J. Bowrey.

III. "On the Temperature at which some of the Alkaloïds, &c., Sublime, as determined by an Improved Method:" by A. W. Blyth.

IV. "On the Detection and Estimation of Free Mineral Acids in various Commercial Products:" by Peter Spence and A. Esilman.

V. "On the Action of Hypochlorites on Urea:" by G. H. Fenton.

VI. "On the Behaviour of Metallic Solutions with Filter Paper, and on the Detection of Cadmium:" by T. Bayley.

VII. "On the Essential Oil of Sage:" by S. Sugiura and M. M. P. Muir.

VIII. "On the Action of Bromine on Sulphur:" by J. B. Hannay.

IX. "On the Determination of High-boiling Points:" by T. Carnelley and W. C. Williams.

X. "On High Melting Points. Part IV:" by T. Carnelley.

XI. "Analogies between the Action of the Copper-zinc Couple and Occluded and Nascent Hydrogen:" by J. H. Gladstone and A. Tribe.

XII. "On the Alkaloïds of the Aconites. Part III:" by C. R. A. Wright and A. P. Luff.

XIII. "On the Alkaloïds of the Veratrums. Part I:" by C. R. A. Wright and A. P. Luff.

XIV. "On the Action of Hydrochloric Acid on various Metallic Salts:" by J. W. Thomas.

XV. "On the Action of Oxides on Salts. Part I:" by E. J. Mills and D. Wilson.

XVI. "On a New Test for Glycerin:" by A. Senior and A. J. G. Lowe.

XVII. "On Ammonium Tri-iodide:" by G. S. Johnson.

XVIII. "Contribution to the History of the Naphthalene Series (No. II, β-Naphthaquinone):" by J. Stenhouse and C. E. Groves.

XIX. "On Pyrotritartaric and Carbo-pyrotritartaric Acids:" by G. Harrow.

XX. "On the Action of Alkaline Hypobromite on Ammonium Salts, Urea, and Oxamide:" by W. Foster.

XXI. "Action of Halogens at High Temperatures on Metallic Oxides:" by C. F. Cross and S. Sugiura.

XXII. "On Manganese Tetrachloride:" by W. W. Fisher.

XXIII. "On the Preparation of Salts of Nitrous Oxide:" by A. E. Menke.

XXIV. "Notes on Madder Colouring Matters:" by E. Schunck and H. Roemer.

XXV. "On the Occlusion of Hydrogen by Copper:" by G. S. Johnson.

XXVI. "On the Part played by Carbon in reducing the Sulphates of the Alkalis:" by J. Mactear.

XXVII. "On the Action of Ethylchlorcarbonate on some Oxygenated Haloid Compounds of the Fatty Series:" by O'Neill F. Kelly.

XXVIII. "Laboratory Notes:" by H. E. Armstrong.

XXIX. "On the Red Colouring Matter of the *Lithospernum Erythrorhizon*:" by M. Richard.

XXX. "A Second Report on some Points in Chemical Dynamics:" by C. R. A. Wright and A. P. Luff.

XXXI. "Note on the Constitution of the Olefine produced by the Action of Zinc upon Ethylic Iodide:" by E. Frankland and L. Dobbin.

XXXII. "On the occurrence of certain Nitrogen-acids amongst the products of the Combustion of Coal-gas and Hydrogen Flames:" by L. T. Wright.

XXXIII. "On the Action of Bromine upon Sulphur:" by J. B. Hannay.

XXXIV. "Researches on Dyeing. Part I. Silk and Rosaniline:" by E. J. Mills and G. Thomson.

XXXV. "Comparison of the Actions of Hypochlorites and Hypobromites on some Nitrogen Compounds:" by H. J. H. Fenton.

XXXVI. "Notes on two new Vegeto-alkaloïds:" by F. Von Müller and L. Rummel.

XXXVII. "On some Fluorine-compounds of Vanadium:" by H. Baker.

XXXVIII. "On the Preparation of Metallic Chlorides:" by C. W. Watts and Chichester A. Bell.

XXXIX. "On the Action of Sodium on the Benzyl Ether of Isobutyric Acid:" by W. R. Hodgkinson.

XL. "On the Determination of Lithia by Phosphate of Soda:" by C. Rammelsberg.

XLI. "A Chemical Study of Vegetable Albinism:" by A. H. Church.

XLII. "Relation between the Melting Points of the Elements and their Coefficient of Expansion:" by T. Carnelley.

XLIII. "A Preliminary Notice on Hydride of Boron:" by F. Jones.

XLIV. "On the Processes for Determining the Organic Purity of Potable Waters:" by C. Meymott Tidy.

XLV. "Researches on the Action of the Copper-zinc Couple on Organic Bodies. (Part IX.) Preparation of Zinc-methyl:" by J. H. Gladstone and A. Tribe.

XLVI. "On the Production of Oxides of Nitrogen by the Electric Arc in Air:" by T. Wills.

XLVII. "On the Action of Alkaline Hypobromite on Oxamide, Urea, and Potassium Ferrocyanide. (Part II):" by W. Foster.

XLVIII. "On the New Hydrocarbons obtained by the Action of Sodium on Turpentine Hydrochloride:" by E. Letts.

XLIX. "On the Formation of Barium Periodate:" by S. Sugiura and C. F. Cross.

L. "On Erbium and Yttrium:" by J. S. Humpidge and W. Burney.

LI. "On the Action of Isobutyric Anhydride on the Aromatic Aldehydes:" by W. H. Perkin.

LII. "On Two New Methods for the Estimation of Carbon: (1) Gravimetric, (2) Chromometric, and their Application to Water Analysis:" by A. Dupré and H. W. Hake.

LIII. "On Stannic Ethide:" by E. Frankland and A. Lawrance.

LIV. "On Aurin. (Part II):" by R. S. Dale and C. Schorlemmer.

LV. "On the Derivatives of Di-isobutyl:" by W. Carleton Williams.

LVI. "Action of Chlorine on Iodine:" by J. B. Hannay.

LVII. "On Colouring-matters derived from Diazo-compounds:" by Otto N. Witt.

LVIII. "Investigations into the action of Substances in the Nascent and Occluded Conditions. Hydrogen (continued):" by J. H. Gladstone and A. Tribe.

LIX. "On some Methods of Vapour-density Determinations:" by J. T. Brown.

LX. "On the Decomposition-products of Quinine and the Allied Alkaloïds:" by J. J. Dobbie and W. Ramsay.

LXI. "On the Quantitative Blowpipe Assay of Mercury:" by G. Attwood.

LXII. "On some Points in the Analysis of Combustible Gases, and in the Construction of Apparatus:" by J. W. Thomas.

LXIII. "On the Action of Isomorphous Salts in exciting the Crystallisation of Supersaturated Solutions of each other, and some Experiments on Supersaturated Solutions of Mixed Salts:" by J. M. Thomson.

LXIV. "On Isomeric Dinaphthyls:" by Watson Smith.

LXV. "On Plumbic Tetrethide:" by E. Frankland and A. Lawrance.

LXVI. "On the Decomposition of Water by certain Metalloïds:" by C. F. Cross and A. Higgin.

LXVII. "On the Volumetric Determination of Chromium:" by W. J. Sell.

LXVIII. "The Production of the Higher Oxides of Iron, Chromium, Manganese, and Bismuth:" by W. Foster.

The following lectures were also delivered:—

"On the Determination of the Index of Refraction of Liquids by means of the Microscope:" by H. C. Sorby, F.R.S., Pres. G.S.

"On the Chemical Aspect of Vegetable Physiology:" by Sidney H. Vines, B.A., F.L.S.

This shows that the recent satisfactory increase in the number of original papers has been well maintained. In the decade from 1859 to 1869 the papers averaged 36 annually, while in the last decade the numbers have been as follows:—

Year ended March,	1870	35	papers.
„ „	1871	32	„
„ „	1872	22	„
„ „	1873	58	„

Year ended March,	1874	....	53 papers.
„ „	1875	....	65 „
„ „	1876	....	66 „
„ „	1877	....	71 „
„ „	1878	....	65 „
„ „	1879	....	68 „

There is an increasing disposition to illustrate the papers read before the Society by experiments; and they have frequently led to interesting discussions. Indeed in one instance a whole evening was given to the consideration of Dr. Tidy's paper, and the remarks of those who were conversant with water analysis. Both these practices—experimental illustration and discussion—are much to be encouraged, not only because they increase the interest and improve the attendance at our meetings, but because an experiment helps greatly the perception and memory of the listener, and controversy rarely fails to bring our conceptions nearer to the facts of nature.

In addition to the discourses already mentioned, we have had the advantage of the Faraday lecture by Professor Wurtz, who chose for his subject "Sur la Constitution de la Matière à l'État Gazeux." It took place on the 13th November, in the theatre of the Royal Institution, which was lighted on that occasion for the first time with the electric light. As Professor Wurtz's discourse is printed *in extenso*, it is not necessary to give any account of it; but those who were present that evening will not readily forget the perfect lucidity of expression with which the lecturer explained his views, the rare manipulative skill with which he performed difficult experiments, or the appreciative enthusiasm with which he described the experiments of others; nor are we likely to forget the simple-hearted friendliness of our guest.

The condition of the Library, and its rules, have been the subject of careful consideration by the Council. Acting on the view that our Library is essentially one of reference, and that therefore the more important works should always be on the shelves at the disposal of Fellows who may wish to consult them, it has been resolved that no serial publication of which the Society does not possess a duplicate copy, shall be taken away from the Rooms. On this account duplicate sets of "Liebig's Annalen," and of the "Annales de Chimie et de Physique" from the commencement of the 3rd series in 1841, have been ordered, and will shortly be placed upon the Library shelves. For the same reason the following journals are now taken in in duplicate:—

"Liebig's Annalen der Chemie."

"Poggendorf's Annalen der Physik."

"Beiblätter zu den Annalen der Physik."
"Annales de Chimie et de Physique."
"Comptes rendus de l'Académie des Sciences."
"Bulletin de la Société Chimique."
"Berliner Berichte."
"Fresenius' Zeitschrift für Analytische Chemie."

The Council have also ordered a large number of new books, and would be glad of the suggestions of Fellows with regard to any others that ought to be added. Arrangements have been made for Fellows at a distance to have books sent to them, on giving a written order and paying the cost of carriage.

The importance of the abstracts which we now publish is universally recognised. In order to facilitate the publication of them, to economise space, and especially to reduce the confusion which arises from different kinds of nomenclature, a new series of instructions to abstractors has been drawn up; and it is hoped that the suggestions adopted, after much consideration, by the Council of our Society, may not be without their influence upon the practice of authors themselves (*see* Appendix III).

During the year every effort has been made to publish both the original papers communicated to the Society, and the abstracts, with as little delay as possible; and thanks to the efforts of our Editors, the Journal has usually been issued to Fellows within the first week of each month.

As complaints have been frequently made as to the ventilation of our rooms, Dr. Russell and Mr. Perkin investigated the matter very fully, and have completely altered the system by which the air is made to circulate through the premises, and with a result highly conducive to our comfort.

A separate report of the Research Fund will be submitted, as was the case last year (*see* Appendix II).

It becomes a matter of consideration in what way the greatest advantage may be obtained from this and other funds available for chemical research. They may sometimes help the most original discoverer, or may sometimes be applied to questions bearing on technology; but I think you will agree with me that they would be peculiarly applicable for the working out of the details of important inquiries, or the accurate determination of chemical constants, work which is extremely necessary, but which has little attraction for the amateur or the man of genius; holds out no prospect of pecuniary gain; and offers but a small meed of reputation as compared with the care and labour which it entails.

Yet, while there is much to encourage in the progress of the past

twelve months, I think I only express the general feeling when I say that we ought not to rest satisfied with present attainments. The Society exists for "the general advancement of chemical science," and this means both the encouragement of research, and the diffusion of the knowledge of new discoveries. With regard to the promotion of research, as our members now exceed 1,000, and the laboratories of our land are growing in importance, we may surely look for a larger amount of original work in coming years; and we should also seek not only to add to previous knowledge, but to increase what I may venture to term the scientific culture of the workers. In our laboratories we are isolated, and are apt to look upon our own pet subject as of prime importance; but when we meet in these rooms, or turn over the pages of our Journal, we are carried away to many different fields of thought in succession: it may be to the production of metals, minerals, or salts, either in nature or by art,—to the wonderful transformation of the carbon compounds, whether in the organisms of plants and animals, or in our own basins or retorts,—or to those borderlands in which the work of the chemist blends with that of the physicist, the geologist, or the physiologist.* This promotes largeness of view, and must react favourably upon the cultivation of our individual corner of the great field. I trust that our Society will never devote its energies too exclusively to one branch of our science; and that it will lay claim to its fair share of physico-chemical researches. Scientific culture will also lead to a perception of what are the higher aims of chemical inquiry. The formation of new compounds is valuable; but we are liable to be encumbered by the richness and quantity of our materials, and to forget the necessity of grouping them together as a part of systematic knowledge. The construction of the most expressive formulæ is useful; but we must be always ready to modify these, as the exigencies of further knowledge may require, in order to get nearer to the truth of nature. We want also to know more of the chemical force itself, and how it acts; not merely what are the products of a reaction, but the steps and intermediate processes, the amount of heat evolved or absorbed, the alteration in volume and in electrical potential, and the time occupied. We want to distinguish those properties which are so profoundly connected with the ultimate molecules of matter, that they are little if at all affected by chemical combination, from those which are the sport of every change. We want to study all the transformations of energy involved in the phenomena of dynamical chemistry, and to determine with precision how the chemical force stands related to the other great forces of nature.

As to the diffusion of chemical knowledge, our Journal is the main

* It may be remarked that the Faraday Lecture, and the two other special discourses of this year, have had reference to these borderlands.

instrument in our hands for effecting this; but the new arrangements in regard to the lending of books from the Library will doubtless advance the same object. It is happily the case that a knowledge of chemistry is fast finding its way into our upper and middle class schools, and though our science is not recognised by the Government Code, many attempts are being made, and not without success, to introduce into our elementary schools some primary knowledge of those facts and principles of nature which lie at the foundation of chemical and physical science. Technical education is also rising into favour, and the formation of a technical college is now engaging the attention of the great City Companies. The Society, as such, can perhaps do but little in this direction, although the practical applications of chemistry are directly alluded to in our charter; but its individual members may accomplish much.

The Foreign Member who has died during the year is M. Malaguti. The ordinary fellows are Messrs. William Baker, Alfred Bird, W. A. Lyttle, W. A. Stewart, and John Wiggin.

Mr. William Baker was born in 1830, and educated in the City of London School; he subsequently turned his attention to science, and entered the Royal School of Mines in 1852, as a student, under Dr. John Percy. In 1855 he went to Sheffield, in the capacity of analytical chemist and manager to Messrs. Barker and Co.'s lead works, with which firm he remained for 15 years. During the last eight years he practised on his own account as an analytical chemist, with which he combined the duties of Borough Analyst to Barnsley and Rotherham, and lecturer on toxicology at the Sheffield School of Medicine. His chief scientific work was in connection with lead, in the desilvering of which he succeeded in removing at the same time any traces of copper by the addition of a little zinc. The purity of the lead thus obtained increased the value of the white lead, made by Messrs. Barker and Co., and of glass makers' red lead, which is also depreciated by the presence of a minute quantity of copper. He also introduced successfully the use of a mixture of acetate of lime and sulphuric acid, as a substitute for acetic acid in the preparation of white lead. In conjunction with Mr. Graham Stuart, he carried on investigations into the presence of nitrogen in steel; and more recently he devoted much attention to the subject of removing phosphorus from iron by means of chlorine and other gases. On the 29th of April last he met with an accident, which terminated fatally on the 6th of June. He was an enthusiastic teacher of science, and was greatly respected by his fellow townsmen, and has left behind him a widow, and a son who was just preparing to follow his father's profession.

Mr. Alfred Bird was born in 1811, his father, Mr. John Bird, being lecturer on astronomy at Eton College. In addition to practising as an analytical and consulting chemist at Birmingham, he devoted considerable attention to physics and meteorology. In the course of his investigations into the laws of sound, he constructed a beautiful set of harmonized glass bowls, extending over five octaves, which he used to play with much skill. In meteorology he devised a plan of demonstrating experimentally that the wind blows in circles. He also, in 1859, constructed a water barometer, a description of which is published in the *Phil. Mag.* for 1865, and which is still in perfect working order. With this he was fond of observing and showing to others the minute oscillations of the atmospheric pressure. He was well known for his originality and as the inventor of several useful appliances. He died December 15, 1878.

Mr. William Auld Stewart, of Apothecaries' Hall, died on September 28th, 1878, at the early age of 34. Born at Campbeltown, in Argyllshire, he received his early education at the Grammar School of which his father was rector. He first devoted himself to pharmacy in his native town, and then removed to Glasgow in order to prosecute the study of chemical science at Anderson's University. He held for a time an appointment in one of the chemical works in that city, but vacated it in 1865, when he came to London, and renewed his scientific studies at King's College. Having completed these, he obtained an important post in the laboratories of Apothecaries' Hall. Some years ago, while superintending the manufacture of bromide of potassium, he accidentally inhaled a large quantity of bromine vapour, which caused extensive hæmorrhage from the lungs, and was the prime cause of his early death. In addition to a sound knowledge of practical chemistry, Mr. Stewart possessed a natural taste for mechanical science, and that happy faculty of invention and adaptation which is of such essential service in chemical manipulation.

Faustino Giovita Mariano Malaguti, whose name has been associated with the University of Rennes for the last 28 years, was born at Bologna on the 15th February, 1802, in which town his father was a pharmaceutical chemist. He entered the university of his native town, and having completed the necessary training at the early age of 16, carried on the business of his father. The political troubles of 1831, however, necessitated his leaving Italy, and he took up his abode in Paris. Here he became acquainted with Gay-Lussac, and was received into his private laboratory along with Pelouze. His work attracted the notice of M. Alexandre Brogniart, and in 1840 he was appointed chemist to the porcelain manufactory at Sèvres, where he contributed greatly towards perfecting the system of carrying on the

works. He devoted much study to the colours used in china painting and to the analysis of kaolin. In 1850 he was elected Professor of Chemistry to the Faculty of Sciences at Rennes; in 1855 he was appointed Dean, and he also held the office of Rector of the Academy until his death. In this new sphere he not only distinguished himself as a Professor of the University, but his books, "Leçons de Chimie Agricole," and "Leçons Élémentaires de Chimie," became the accepted text books in other scientific centres, on account of their clearness, precision, and soundness of information, and his scientific investigations extended over a wide range of subjects. Of his published papers, "Poggendorff's Biographical Dictionary" furnishes a list of 40 (some conjointly with M. Durocher and others), dealing with organic and inorganic chemistry, and its relations to agriculture and geology. In addition to those connected with his work at Sèvres, he bestowed much attention on the presence of silver and lead in sea-water; on the association of silver with other ores; on the production of pyrites in alluvial earths; and on hydraulic cements. In organic chemistry, the great discussion of his earlier days on the theory of substitution could not fail to attract his attention, and he made numerous investigations with the object of bringing it to the test of experiment. His studies of the chloric ethers are models of careful and intelligent work, and the results arrived at by him contributed greatly to the settlement of the theory which had been so warmly disputed. This was not the only question connected with chemical philosophy which he examined. He experimented upon the reciprocal action of soluble salts, and determined and tabulated what he called "coefficients of decomposition;" and he also investigated the action that takes place between various soluble and insoluble salts.

Malaguti became a naturalised Frenchman, and married into a French family. In 1850 he received the degree of Doctor in Science; in 1855 was elected corresponding member of the French Academy; and in 1860 was appointed Officier de la Legion d'Honneur. He also received the decoration of the Order of St. Maurice and Lazare; and was enrolled among the honorary members of the Academy of Turin and other learned bodies. He died at Rennes on the 26th April, 1878, respected not only for his scientific attainments, but for the worth of his private life.

Dr. Armstrong then read a list of grants from the Research Fund, made during the past year (see Appendix I).

Dr. Odling then moved a vote of thanks to the President and the adoption of his report. It was very gratifying to hear such a flourishing report, and he thought the Fellows might congratulate themselves on having had such a President.

Mr. NEISON, in seconding the motion, urged that a copy of the General Index should be presented to every Fellow of the Society.

Dr. WRIGHT suggested that the hours during which the Library was open in the evening should be extended from seven to nine to seven to ten.

The motion was then carried by acclamation.

The PRESIDENT felt greatly honoured by the cordial manner in which the motion had been received, and the kind way in which Dr. Odling had introduced it. He had experienced much pleasure during his occupation of the chair, which any chemist would be proud to occupy. He was very grateful for the way in which the Council and the Society had seconded him in everything.

The TREASURER (Dr. Russell) then read his account of the finances of the Society. The state of the Society was very satisfactory. The income for the year was £2,350; the expenditure £2,300. The balance in hand of the Research Fund amounted to about £230 (see page 270).

Mr. FRISWELL then read the report of the Auditors, Messrs. Spiller, Thomson, and Friswell (see page 272).

Dr. THUDICHUM had listened with great satisfaction to the statement of the Treasurer. After making a few remarks as to the present method of electing Fellows, Dr. Thudichum proposed a cordial vote of thanks to the Treasurer, who had performed his important duties in the most perfect manner the Society could wish.

Dr. GILBERT seconded the motion, which was carried unanimously, with much pleasure.

Dr. RUSSELL returned thanks to the meeting.

Mr. NEISON proposed a vote of thanks to the Officers and Council.

This was seconded by Mr. GROSJEAN, and carried unanimously.

Mr. PERKIN replied.

Votes of thanks were subsequently given to the Auditors, the Editors, the Abstractors, and the Reporter of the Society.

The following Officers were then announced from the chair as having been duly elected for the ensuing year:—

President.—Warren De La Rue, D.C.L., F.R.S.

Vice-Presidents.—F. A. Abel, C.B., F.R.S.; Sir B. C. Brodie, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; F. Field, F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; N. S. Maskelyne, F.R.S.; H. E. Roscoe, Ph.D., F.R.S.; R. Angus Smith, Ph.D., F.R.S.; J. Young, F.R.S.

Secretaries.—W. H. Perkin, F.R.S., and H. E. Armstrong, Ph.D., F.R.S.

Foreign Secretary.—Hugo Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of Council are.—M. Carteighe; A. H. Church; W. N. Hartley; C. W. Heaton; E. Riley; W. C. Roberts; W. A. Tilden; W. Thorp: T. E. Thorpe; J. L. W. Thudichum; R. V. Tuson; R. Warington.

Dr. The Treasurer in Account with the Chemical Society from March 27, 1878, to March 23, 1879. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 27th, 1878	861	15	10			
,, in hand of Treasurer	4	3	7			
				865	19	5
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 22nd, 1878, to March 20th, 1879, inclusive.						
7 Life Compositions	130	0	0			
61 Admission Fees	244	0	0			
3 Subscriptions for 1875	6	0	0			
11 ,, ,, 1876	22	0	0			
34 ,, ,, 1877	64	0	0			
161 ,, ,, 1878	316	0	6			
630 ,, ,, 1879	1,044	12	0			
1 ,, ,, 1880	2	0	0			
1 ,, ,, 1881	2	0	0			
				1,830	12	6
Sale of Journal	319	13	11			
,, Index	4	13	6			
				324	7	5
Subscriptions for Proceedings of Royal Society, vols. 27 and 28				77	10	0
From Society of Public Analysts for Gas, Coal, &c.	3	0	0			
From Institute of Chemistry	9	16	0			
				12	16	0
Dividends on Consols (£4,000)	117	10	0			
,, Metropolitan Board of Works 3½ per cent. Stock	47	3	11			
,, London and North Western Railway Debenture Stock	30	18	6			
				195	12	5
Legacy from Sidney Ellis, Esq. (amount received)				1,000	0	0
Assets.	£	s.	d.			
Balance at Coutts'	1,964	9	5			
,, in hands of Treasurer	0	4	9			
Three per cent. Consols	4,000	0	0			
London and North Western Railway Debenture Stock	788	0	0			
Metropolitan Board of Works 3½ per cent. Stock	1,500	0	0			
				4,306	17	9

	£	s.	d.	£	s.	d.
Expenses on Account of Journal.						
Salary of the Editor	250	0	0			
,, Sub-Editor	100	0	0			
Fees to Abstractors of Papers	240	19	3			
Incidental expenses of Editor	2	10	0			
Periodicals for use of Abstractors	30	5	9			
Distribution of Journal	168	9	8			
Printing of Journal	823	17	6			
				1,616	2	2
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	72	13	4			
Binding Books and Periodicals	40	9	2			
				225	2	6
Printing Authors' Copies				30	0	8
Royal Society's Proceedings				59	8	9
Reports of Meetings				25	10	0
Miscellaneous Printing				45	3	6
Insurance of Society's Furniture and Books				2	0	0
Stationery, Postage, Envelopes, Obligation and Receipt Books				25	5	4
Inhabited House and Income-tax				6	17	6
Collector's Commission on Subscriptions				91	10	0
Treasurer's Stamps and Clerical Aid				5	8	0
Chemicals for Preparation-room				3	9	7
Expenses in connection with the Faraday Lecture.						
Printing, Postages, and Expenses at Royal Institution	10	0	6			
Preparation of Medal and Case	2	0	0			
Honorarium to Lecturer	20	0	0			
Translating Lecture	3	0	0			
				35	0	6
House Expenses.						
Repairing, Gas Fittings and Meter, and purchase of Tea Urn	8	18	11			
Repairing Boiler to Hot Water Apparatus	1	15	6			
Making Additional Shelves in Library	3	1	6			
Providing Refreshments at Meetings	23	8	3			
Heating of Building	17	17	0			
Lighting of Building	45	7	9			
Cleaning of Building	20	0	0			
Wages of House Porter	39	8	0			
Petty House Expenses	9	6	2			
Gratuity to Gate Porter	2	2	0			
				171	5	1
Petty Cash Disbursements				0	4	9
Balance in Bank	1,963	5	1			
,, in hands of Treasurer	1	4	4	1,964	9	5
				4,306	17	9

Examined and found correct, March 25th, 1879. { John M. Thomson, John Spiller, R. J. Friswell, } *Auditors.*

		1,963	5 1
„	in hands of Treasurer	1	4 4
		1,964	9 5
		4,306	17 9

Examined and found correct, March 25th, 1879. JOHN M. THOMSON, JOHN SPILLER, R. J. FRISWELL, *Auditors.*

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.

FROM MARCH 27, 1878, TO MARCH 25, 1879.

DR. **CR.**

	£	s.	d.
Balance at Bank, March 27, 1878	219	7	0
Subscriptions and donations	227	6	0
Dividend on North British Railway Stock	39	7	10
„ Metropolitan 3½ per cent. Stock	99	12	1
	£585	12	11

		£	s.	d.
1878.				
Aug. and Sept.	By grants made	160	0	0
1879.				
Feb. and Mar.	By grants made	90	0	0
	By balance at Bankers	335	12	11
		£585	12	11

Assets.	£	s.	d.
North British Railway 4 per cent. Preference Stock	1,000	0	0
Metropolitan Board of Works 3½ per cent. Stock	2,900	0	0
Balance at Bankers	335	12	11
	£4,235	12	11

Examined and found correct, 25th March, 1879,

JOHN M. THOMSON,
JOHN SPILLER,
RICHARD JOHN FRISWELL, } *Auditors.*

Appendix I.

AUDITOR'S REPORT.

To the President and Council of the Chemical Society.

Gentlemen,

Having been entrusted with the duty of auditing the Treasurer's Accounts, we have the honour to report that we met Dr. Russell on Tuesday last, 25th instant, and went through his books, comparing the entries with the separate vouchers, and have signed both the General Cash Statement and "Research Fund" Account as being correct.

We have since made enquiries of the Chief Accountant, Bank of England, and of the Manager of Messrs. Coutts and Co.'s Bank, and find that the undermentioned Investments are actually in possession of the Society, viz.:—

£4,000 Three per cent. Consols.

£4,400 Metropolitan Board of Works 3½ per cent. Stock.

£788 London and North Western Railway Debenture Stock.

£1,000 North British Railway Preference Stock.

We presume it will be the intention of the Council to invest, at an early date, part of the very large Cash Balance now standing as "Current Account" at Messrs. Coutts and Co.'s Bank (over £1,900).

Attesting to the very satisfactory state of the Society's finances, and to the care bestowed upon them by the Treasurer,

We remain,

Gentlemen,

Your obedient Servants,

John Spiller,
John M. Thomson,
R. J. Friswell,
} *Auditors.*

London, March 29th, 1879.

Appendix II.

REPORT OF THE RESEARCH FUND COMMITTEE.

Since the last Annual Meeting of the Society the following sums have been granted from the Research Fund by the Council on the recommendation of the Research Fund Committee:—

£50 to Mr. Hartley, for an investigation of the Absorption of the Ultra-Violet Rays of the Spectrum by Organic Substances.

£30 to Dr. W. Ramsay, for determining the Electric Conductivity and Resistance of Solutions of Salts at different Temperatures.

£50 to Dr. W. A. Tilden, for an investigation into the Chemical Nature of the Terpenes.

£10 to Mr. W. A. Shenstone, for an examination of certain Reactions of Brucine and Strychnine.

£20 to Mr. W. Jago, for a research on the Organic Matter in Seawater.

£20 to Mr. Francis Jones, for the investigation of Boron Hydride.

£15 to Mr. F. D. Brown, for the experimental study of the Theory of Fractional Distillation.

£10 to Dr. C. A. Burghardt, for the investigation of the Constitution of Topaz.

£15 to Prof. Thorpe, for the investigation of Abietene, the Hydrocarbon of the Nut Pine.

£30 to Dr. Dupré, for the estimation of the Organic Carbon in Atmospheric Air.

During the past session several gentlemen who have received grants have communicated papers to the Society, viz., Mr. Johnson (1878, p. 397), Dr. Harrow (1878, p. 425), Dr. Wright (in conjunction with Mr. Luff, 1878, p. 504), and Mr. Carleton Williams (1879, p. 125).

Mr. Hartley (in conjunction with Mr. Huntington) has presented the first results of the investigation of the action of organic substances in absorbing the ultra-violet rays of the spectrum to the Royal Society (*vide* Proceedings, vol. 28, p. 233). The conclusions arrived at are briefly as follows:—

(1.) The normal alcohols of the $C_nH_{2n+1}.OH$ series are remarkable for transparency to the ultra-violet rays, pure methylic alcohol being as nearly so as water.

(2.) The normal fatty acids exhibit a greater absorption of the more refrangible rays of the ultra-violet spectrum than the normal alcohols containing the same number of carbon atoms.

(3.) There is an increased absorption of the more refrangible rays

corresponding nearly to each increment of CH_2 in the molecule of the alcohols and acids.

(4.) Like the alcohols and acids, the ethereal salts derived from them are highly transparent to the ultra-violet rays, and do not exhibit absorption-bands.

(5.) Benzene, and the hydrocarbons, phenols, acids, and amines derived therefrom, are remarkable—firstly, for their powerful absorption of the ultra-violet rays; secondly, for the absorption-bands made visible by dissolving them in water or alcohol and diluting; and thirdly, for the extraordinary intensity of those absorption-bands, that is to say, their power of resisting dilution.

(6.) Isomeric bodies containing the benzene nucleus exhibit widely different spectra, inasmuch as their absorption-bands vary in position and in intensity.

(7.) The photographic absorption spectra can be employed as a means of identifying organic substances, and as a most delicate test of their purity.

The Research Fund Committee have received the following reports of the progress made by those gentlemen who have not yet communicated papers to the Society:—

Dr. Crow states that he has obtained entirely negative results. Thus he finds that vanadium tetrachloride is reduced to the trichloride by zinc-ethyl, and that the trichloride is not at all acted upon. Vanadium oxychloride also does not exchange chlorine for ethyl when submitted to the action of zinc-ethyl. No result was obtained by acting on sodium ethylate with $VOCl_3$, or on silver vanadate with ethyl iodide. It would appear therefore that vanadium does not form organic compounds corresponding with those of nitrogen, phosphorus, &c.

Dr. Carnelley has investigated the action of heat on the mixed vapours of benzene and toluene, and has obtained diphenyl, ditolyl, phenyltolyl, anthracene, phenanthrene, and a new hydrocarbon. The oxidation-products and a number of substitution derivatives of phenyltolyl and of ditolyl have been investigated, and Dr. Carnelley hopes soon to communicate the results to the Society.

Mr. Bedson reports that, from his investigation of some of the already known derivatives of phenylacetic acid, he concludes that they are mixtures of isomeric bodies.

Dr. Armstrong states that he has examined the products of the action of a variety of so-called dehydrating agents on camphor, and has obtained results which both extend and correct those of previous workers in this field, and that he has prepared a considerable number of highly characteristic derivatives of camphor, and finds that the product of the action of iodine on the terpenes largely consists of a saturated hydrocarbon, which appears to be identical with that

obtained by Mr. Gaskell and himself by digesting camphor with iodine; and that apparently the same hydrocarbon is present in very small quantity in all terpenes; also that, in conjunction with Dr. Tilden, he has made an exhaustive examination of the action of sulphuric acid on a number of terpenes and of the nature of so-called terebene. He proposes to lay his results before the Society at an early date.

Mr. NEISON reports that he has been unable to make much progress, owing to his having met with a serious accident and to the pressure of business engagements.

Dr. TILDEN states that he has prepared a number of terpenes in a state of purity and that he has determined their physical properties, and also prepared and examined some of their derivatives; that he has made further experiments on the production of terpin and terpinol and their relations to each other and to the terpenes; that in connection with this matter a partial examination of rosin oil and spirit has been made; and that, in conjunction with Dr. Armstrong, a very careful investigation has been made of the conditions under which Riban's terebene is produced from turpentine, and of the true characters of this remarkable substance. It is proposed to extend these experiments on the action of sulphuric acid to the terpenes generally.

Mr. SHENSTONE reports that he has been unable to advance his experiments, in consequence of the apparent unfitness of commercial brucine for the purposes of his work, and the delay which has arisen in extracting the alkaloïd by a process whereby the possibility of decomposition was excluded.

Dr. RAMSAY reports that he has made some progress in ascertaining the resistance of solutions of certain salts, although less than he had wished, as he had been unable regularly to obtain the use of the battery in the Physical Laboratory during the winter session; he expects to have greater opportunity in the coming months when there are no classes.

Mr. JAGO reports that he has as yet been able only to make the preliminary arrangements for his experiments, as he has not received the required gas-analysis apparatus.

Appendix III.

INSTRUCTIONS TO ABSTRACTORS.

To _____

With each paper or batch of papers forwarded to you for abstraction a printed notice will be sent, requesting you to return the paper or papers at once to me if you cannot complete the abstract within days, and the Council instruct me to beg that you will pay particular attention to this request.

The Council request that, in preparing abstracts for the Society's Journal, you will be guided as far as possible by the following rules and suggestions.

H. Watts, *Editor.*

"1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

"2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

"3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

"4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, have already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for reference, thus:—*Dingl. polyt. J.*, **221**, 92, instead of ccxxi, 92.

"5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

"6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

"7. Equations, as a rule, should *not* be written on a separate line, but should 'run on' with the text. Simple reactions involving a mere interchange of radicles, or the withdrawal or addition of a particular element or group of elements, need not generally be expressed by equations.

"8. Employ names such as sodium chloride, potassium sulphate,

ethyl acetate, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle, *e.g.*, mercurous and mercuric chloride, sulphurous and sulphuric acid.

"9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride or sulphur trioxide. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen-sodium sulphate, hydrogen-disodium phosphate, &c., to the acid salts. As a rule, it is best merely to give the *formulæ* of basic salts.

"10. To economise space, it is desirable, (1) that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; (2) that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2.CH_2.CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, $\bar{A}c$ for $CO.CH_3$, and $\bar{B}z$ for $CO.C_6H_5$; and (3) that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$CCl_3.CH(OEt)_2$ instead of $CCl_3—CH\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$

$(CCl_3.CH.OH)_2S$ instead of $\begin{matrix}CCl_3—CH—OH\\CCl_3—CH—OH\end{matrix}\!\!\rangle S$

$CH_2:CH_2$ instead of $CH_2{=}CH_2$

$CH:CH$ instead of $CH{\equiv}CH$

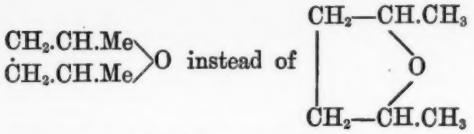
$CH:C.CH_2.CH_2.C:CH$ instead of $\begin{matrix}CH_2—C{\equiv}CH\\|\\CH_2—C{\equiv}CH\end{matrix}$

$MeCH:CHPr^{\alpha}$ instead of $CH_3.CH{=}CH.CH_2.CH_2.CH_3$

$COOH.CH:CMe.COOH$ instead of $\begin{matrix}CH_3—C{=}CH\\|\quad\;|\\COOH\;\;COOH\end{matrix}$

$CH_2Br.CBrMe_2$ instead of $\begin{matrix}CH_3\;\;CH_3\\\diagdown\;\;\diagup\\CBr\\|\\CH_2Br\end{matrix}$

$\bar{A}c.CEt_2.COOEt$ instead of $\begin{matrix}CH_3\\|\\CO\\|\\C\langle C_2H_5\\\quad\;\diagdown C_2H_5\\|\\COOC_2H_5\end{matrix}$

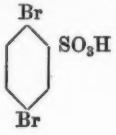


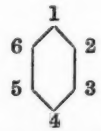
$C_6H_5CH(O\overline{Bz}).CH(O\overline{Bz}).COOEt$ instead of
$C_6H_5.CH(O.CO.C_6H_5).CH(O.CO.C_6H_5).COOC_2H_5$.

"11. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3.(CH_2)_x.CH_3$. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane: for example, $CH_3.CH_2.CH_2.CH_3$ = propylmethane; $CH_3.CH(CH_3)_2$ = isopropylmethane or trimethylethane; or, although less frequently, by names such as diisopropyl.

"12. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Distinguish the homologues of ethylene whenever possible by names indicating their relation to it, such as methylethylene, dimethylethylene, &c., denoting the di-derivatives of the form $C_nH_{2n+1}.HC:CH.C_nH_{2n+1}$ as α-, and those of the form $CH_2:C(C_nH_{2n+1})_2$ as β- compounds: thus, $CH_3.CH:CH.CH_3$ = α-dimethylethylene; $CH_2:C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH:C.C_nH_{2n+1}$ and $C_nH_{2n+1}.C:C.C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2:C:CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

"13. In representing the constitution of benzene derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, as in the following example:

Paradibromobenzenesulphonic acid, $C_6H_3Br_2.SO_3H$ [Br : SO_3H : Br = 1 : 2 : 4] instead of 

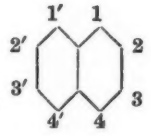
the figures always being used in the order 

Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as

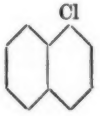
1 : 2 dibromobenzene, 1 : 3 dibromobenze, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

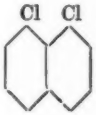
"14. In representing the constitution of derivatives of other 'closed chain' hydrocarbons also, as rule, do not employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

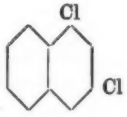
"*In the case of naphthalene*, express the position of the radicles introduced in place of hydrogen relatively to the carbon atoms common to the two 'rings,' and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:

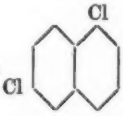


"The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene [Cl : Cl = 1 : 2], &c., thus:—

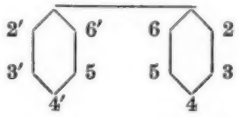
1 : 2 dichloronaphthalene = 

1 : 1′ dichloronaphthalene = 

1 : 3 dichloronaphthalene = 

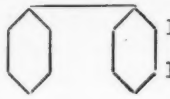
1 : 3′ dichloronaphthalene = 

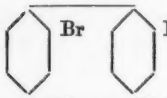
"*In the case of diphenyl*, indicate the position of the radicles relatively to the carbon atom of the one C_6-group which is associated with the other C_6 group, and number the positions in the one group by the figures 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′, as shown by the following symbol:



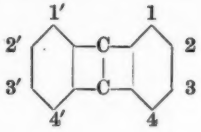
Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

and the two dibromodiphenyls  and

 are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6′].

"*In the case of anthracene*, employ the following symbol, and indicate the position of the radicles relatively to the central C_2– group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].
Purpurin $C_6H_4 : C_2O_2 : C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

"In speaking of compounds such as these, their constitution may be represented by the names

1 : 2 Dihydroxyanthraquinone		= Alizarin.
1 : 4	,,	= Quinizarin.
2 : 3′	,,	= Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone		= Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed chain hydrocarbons in square brackets.

"15. Distinguish all alcohols, *i.e.*, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*, *e.g.*, quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol; furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5.OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl, anethoïl.

"Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

"16. Bodies such as the acids of the lactic series containing the group (OH) should be termed *hydroxy-*, and not oxy-derivatives, *e.g.*, hydroxyacetic and not oxyacetic acid. Compounds containing the

analogous groups C_2H_5O, C_6H_5O, $CH_3.COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyllactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2.COOH$, and not $C_6H_3(OC_2H_5)_2.COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2.COOH$.

"17. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 15).

"18. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic acids*, or, failing this, sulpho-compounds: as benzenesulphonic acids, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2.NH_2$ should be termed sulphonamides.

"19. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, *e.g.*, palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide, should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate."

The Editor's decision in all matters connected with the Abstracts must be considered final.

XXXIII.—*On Lead Tetrachloride.*

By W. W. Fisher, M.A., Aldrichian Demonstrator of Chemistry, Oxford.

The existence of a tetrachloride of lead has been for many years generally assumed upon theoretical grounds, but direct experimental evidence has not hitherto been obtained to establish the composition of this interesting compound. It seemed to me possible that the method of analysis adopted to prove the existence of a tetrachloride of manganese would be suitable also for the analogous lead compound, and, as the result shows, this supposition was entirely verified by experiment. (See this Journal, 1878, xxxiii, 409.)

When lead dioxide is acted upon by moderately strong hydrochloric acid, a yellow solution is obtained smelling strongly of chlorine, which is decomposed by heat, with evolution of chlorine gas, while ordinary lead chloride is deposited in the crystalline form. This yellow solution gives a precipitate of brown hydrated peroxide of lead when treated with solutions of the fixed alkalis or alkaline carbonates, and also with oxides and carbonates not freely soluble in water, such as oxides of magnesium, zinc, mercury, and lead, and carbonates of barium, manganese, lead, and many other metals. Moreover, compounds of the alkalis with weak acids, such as acetic and boracic acids, similarly produce a precipitation of hydrated peroxide of lead. It is remarkable, too, that if excess of hydrochloric acid is avoided, and the liquid is carefully saturated with lead dioxide, the yellow solution, by simple dilution with pure water, is decomposed, and the same precipitation of lead dioxide observed, precisely as the solution of manganese tetrachloride is decomposed by the addition of water.

The method of experiment was the same as that followed in the analysis of the similar manganese compound, and the same apparatus was employed for performing the filtration with least possible loss of chlorine. But as the total chlorine could not conveniently be determined by means of the decomposition of potassium iodide, a solution of a ferrous salt of known strength was used in this case.

A quantity of lead dioxide was cautiously added to twice its weight of hydrochloric acid previously diluted with an equal volume of water. The yellow solution thus prepared was after a few minutes poured off from the precipitated protochloride of lead and treated as follows:—

A. 20 c.c. were withdrawn by a pipette and allowed to flow into a solution of acetate of soda, whereby a precipitate of peroxide of lead was obtained.

B. 20 c.c. were withdrawn by a pipette and added to a definite volume of ferrous sulphate of known strength in excess.

After a few minutes the sample A was filtered into a Woulffe's bottle by means of the apparatus already described in my former paper. The peroxide of lead upon the filter was washed, dried, and ignited, and the weight of lead calculated from the protoxide thus obtained. A small quantity of free chlorine present in the filtrate was estimated, after addition of potassium iodide, by standard sodium hyposulphite. The filtrate did not contain lead.

The sample B was titrated with a solution of potassium permanganate, and from the excess of ferrous salt left in the liquid the amount of chlorine used in oxidation could be calculated. Since, however, a small quantity of free chlorine invariably passed through the filter from the operation A, this amount had to be subtracted from the total chlorine deduced from operation B.

If we assume the reactions to take place as follows :—

$$\text{I. } PbO_2 + 4HCl = PbCl_4 + 2H_2O,$$
$$\text{II. } PbCl_4 + 2H_2O = PbO_2 + 4HCl,$$
$$\text{III. } PbCl_4 = PbCl_2 + Cl_2,$$

it is evident that the lead obtained in the second equation (*i.e.*, operation A) stands to the chlorine obtained in the third equation (*i.e.*, operation B) in the ratio of 207 to 71, or 1 atom of lead to 2 atoms of chlorine.

The following numbers were obtained in the several experiments :—

Oxide of lead	·2947 gram
Chlorine	·0857 „

whence Pb : Cl = 1 : 1·97.

Oxide of lead	·5714 gram
Chlorine	·1679 „

whence Pb : Cl = 1 : 2·03.

Other experiments gave the ratios 1 : 1·98 and 1 : 1·96.

There is no doubt whatever that the yellow solution thus examined contains a compound of lead with chlorine in the proportion of 1 atom of lead to 4 of chlorine. And as the filtrate from the sodium acetate is free from lead, except in mere traces, such a solution is practically nothing else than the tetrachloride of lead in excess of hydrochloric acid.

Action of Hydrochloric Acid upon Red Lead.

When red lead is treated with a small quantity of hydrochloric acid, it darkens in colour and is converted into a mixture of lead protochlo-

ride and lead dioxide. The further addition of hydrochloric acid dissolves the dioxide, and gives a yellow liquid identical in all respects with the solution described above. This fact is of considerable interest as being exactly comparable with the action of hydrochloric acid upon the so-called red oxide of manganese.

$$Pb_3O_4 + 8HCl = PbCl_4 + 2PbCl_2 + 4H_2O.$$
$$Mn_3O_4 + 8HCl = MnCl_4 + 2MnCl_2 + 4H_2O.$$

Action of Chlorine upon Lead Chloride.

Chloride of lead in the dry state is not acted upon by chlorine, but when suspended in dilute hydrochloric acid or solution of potassium or sodium chloride becomes converted into the perchloride by the passage of the gas through the solution. The solution so formed, in the case of hydrochloric acid, is identical in all respects with the yellow liquid already described. When, however, an alkaline chloride is used, the solution, from the absence of excess of acid, is more readily decomposed by water. Sulphuric acid and solution of alkaline sulphate give precipitates of lead sulphate only after some time, but with a warm saturated solution of sodium sulphate, a precipitate of *lead peroxide* is thrown down.

Sobrero and Selmi have investigated this subject (*Ann. Chim. Phys.* [3], **29**, 165) and obtained a compound $PbCl_4$,9NaCl, while Nicklès (*ibid.* [4], **10**, 323), by the use of calcium chloride, obtained a compound $PbCl_4$,16$CaCl_2$.

When a current of chlorine gas is passed into water containing lead chloride, there is at first no change apparent beyond a slight dissolution of chlorine. The liquid remains colourless, and yields with alkalis a precipitate of hydrated protoxide of lead almost white in colour. After some hours, however, if the passage of the gas be continued, a yellow solution of lead tetrachloride is obtained with simultaneous deposition of a coating of lead dioxide on the walls of the flask containing the liquid, which it should be noted has now become strongly acid. The chlorine gas used was carefully purified with anhydrous copper sulphate to remove all free hydrochloric acid, and some experiments were conducted in the dark; but as the result was in every case the same, it is evident that the acid is one of the products of the reaction,

$$PbCl_2 + Cl_2 + 2H_2O = PbO_2 + 4HCl.$$

It is probable that lead tetrachloride is first formed, and continually decomposed by the water present, until the acid liberated in the solution is sufficient to keep it in a stable condition. All the experimental evidence points to the conclusion that the higher chloride of lead is

unstable in the presence of water alone, but may exist as a double salt in the presence of other chlorides. Indeed the yellow liquids above described may be kept for several months in ordinary stoppered bottles. It is not possible to obtain any double salts by evaporation, but I think the solution contains lead as chloroplumbate, H_2PbCl_6, or K_2PbCl_6, and I am endeavouring to establish this point by further experiments.

Quantitative Estimation of Lead.

The conversion of lead-salts into peroxide by means of a current of chlorine, appears to afford in principle a useful analytical method. A solution of lead nitrate is but slightly acted on by chlorine (a perceptible quantity of peroxide is formed after some time), but in the presence of sodium acetate the precipitation appears complete. Lead acetate with chlorine is also converted into peroxide. As bromine water is a more convenient agent than chlorine gas for analytical purposes, I attempted to substitute one for the other, and, as the following experiments show, with entirely satisfactory results:—

A. 1·5395 grams of lead acetate, with excess of sodium acetate, were treated with bromine in cold water. After filtration the precipitated lead peroxide was ignited, and gave ·9074 gram protoxide of lead. This equals 54·71 per cent. of lead.

B. ·4320 gram acetate of lead, with acetate of soda and bromine water slightly warmed, gave ·2538 gram of lead protoxide, which corresponds to 54·67 per cent. of lead.

C. 1·0615 grams acetate of lead, heated with sulphuric acid, gave ·8495 gram of lead sulphate, indicating 54·79 per cent. of lead. The theoretical quantity of lead in the pure salt is 54·67 per cent.

This method, therefore, furnishes a satisfactory means for the quantitative estimation of lead in cases where the use of sulphuric acid may happen to be undesirable.

I wish to express my thanks to Mr. V. H. Veley, of University College, for the care with which he has performed most of the quantitative work connected with this investigation.

XXXIV.—*On Terpin and Terpinol.*

By William A. Tilden.

Crystallised Terpin.

I have little to add to my former statements regarding the preparation of this compound. As already mentioned in my preliminary paper (*Chem. Soc. J.*, June, 1878), the hypothesis of the formation of a compound of terpinol with the elements of a nitrate and its continuous decomposition by the water, is in accordance with the facts observed, and serves to explain the formation of terpin.

The liquid left after the deposition of crystals has gone on for some time, undoubtedly contains terpinol, recognisable by the action of hydrochloric acid and of sulphuric acid, as described further on. It also contains a nitrate or the compound of terpinol with a nitrate, for after washing thoroughly with water and distilling in steam, the yellowish oil obtained gives ammonia by the action of reducing agents, and when heated evolves nitrous fumes. In one instance the liquid which had been exposed to the air some months, and had almost ceased to deposit crystals of terpin, was washed and distilled in steam, but on attempting to distil it alone, a violent reaction set in, attended by evolution of red fumes, and in a few minutes the liquid burst into flame.

Attempts to substitute other acids for nitric acid in this process failed. Dilute sulphuric acid seems to produce no effect; and the same negative result attended experiments with acetic acid and alcohol, either in the cold, or after heating, till there was a strong smell of acetic ether; also with hydrochloric acid and alcohol, with or without the addition of chloride of zinc.

The terpentin hydrate, $C_{10}H_{18}O$, described by Deville as an occasional product of the nitric acid process for the preparation of terpin, appears to be nothing but terpinol. In my experience, however, the liquid which is in the act of depositing crystals, is always nearly destitute of rotatory power.

I must modify my former statement that terpin is not obtainable from the terpenes of the orange group. From hesperidene, the terpene of orange oil, I have never obtained a trace of crystallised substance, a black tarry matter being the sole product. But from essence of lemon I find that crystals can be abundantly produced. This agrees with the published statements of Deville, but until quite recently I was always of opinion that this was due to the lævogyrate turpentine present as a natural constituent of pure essence of lemon. (See *Pharm. J. Trans.*, February, 1879, p. 654.) I have, however, made compara-

tive experiments with great care upon the purified lemon hydrocarbon (b. p. 174—6°), and have come to the conclusion that the terpin obtained is really produced from that substance. Lemon differs from orange in other respects, notably in the amount of cymene obtainable from the dibromide (Wright, *Chem. Soc. J.*, November, 1877), and as I have found, in its behaviour with sulphuric acid, so that I am now satisfied that they are entirely distinct, and that the differences observed between the two hydrocarbons are not due simply to impurity.

Crystals of terpin hydrate prepared from the pure terpenes of American and French turpentine oils and from lemon oil have been submitted to Professor Maskelyne, and are pronounced by him to be identical (*Phil. Mag.*, February, 1879).

Terpinol.

The preparation and chief properties of this substance were described in the preliminary paper, but the question whether the formula $C_{10}H_{18}O$ should be finally adopted, or whether it ought to be doubled, was left unsettled. The vapour-density of the compound has since been twice taken by Hofmann's method. The specimen employed had been re-distilled between 205° and 215°. The following results were obtained :—

I.	Weight of liquid	·0210 gram.
	Temperature of the air	16°.
	Barometer before introduction of the bulb	744 mm.
	Barometer after introduction of the bulb, and heated to 186°	657 mm.
	Volume occupied by the vapour	50·4 c.c.
II.	Weight of liquid	·0156 gram.
	Temperature of the air	18°.
	Barometer at commencement	754 mm.
	Barometer at end	715 mm.
	Temperature of vapour	185°.
	Volume of the vapour	76·2 c.c.

The vapour-densities calculated from these results are as follows :—

I.	II.
63·8	62·3

The formula $C_{10}H_{18}O$ corresponds with a vapour-density of 77. It is clear, therefore, that the formula is not a multiple of this, and the low number obtained in these two experiments must be ascribed to partial dissociation of the vapour into a hydrocarbon, $C_{10}H_{16}$, and water.

This hypothesis is confirmed by other observations. Thus the percentage of carbon contained in the substance is in excess of the numbers required for the formula $C_{10}H_{18}O$, and after distillation the amount is slightly increased.

	Terpinol distilled in steam.	Terpinol distilled alone between 205° and 215°.	Theory for $C_{10}H_{18}O$.	Theory for $C_{10}H_{16}$.
C..	78·3	78·9	77·9	88·2
H..	12·2	11·9	11·7	11·8

The boiling point, moreover, is not constant, but ranges through about 10° or 12°.

Terpinol is not changed by sodium amalgam acting upon the alcoholic solution, but it will dissolve one atom of sodium forming a white pasty substance, from which terpinol is regenerated by the action of water. The sodium derivative resinifies when exposed to air or oxygen, without producing any definite acid. Terpinol may be assumed, from the action of sodium, to contain hydroxyl, but attempts to prepare from it an ether by the action of acetic anhydride have not been successful.*

It is, however, acted upon by the stronger acids very promptly. Hydrochloric acid gas passed into the liquid is absorbed and soon produces an intense purple coloration, which, by further action of the gas, fades, and a mass of colourless crystals is produced, consisting of the dihydrochloride, $C_{10}H_{18}Cl_2$, which melts at 48°.

It is somewhat remarkable that this chloride, thus formed from terpinol, corresponds in constitution not with that substance, but with terpin—

$$C_{10}H_{18}\begin{cases}Cl\\Cl\end{cases} \qquad C_{10}H_{18}\begin{cases}OH\\OH\end{cases}$$

although when decomposed by alkalis, it yields terpinol, and not terpin.

At first sight this appears to suggest that terpinol stands to terpin in the relation of an anhydride, and that its production by saponification of the chloride is analogous to the production of mannitane from the ethers of mannite. On the other hand, the formation of terpinol from terpin by the action of dilute acids closely resembles the formation of pinacolin from pinacone by the same agents, and there is a general resemblance of terpin to pinacone and of terpinol to pinacolin. Pinacolin has, however, been shown to be a ketone, whilst terpinol presents none of the characters of a ketone beyond the property of yielding by oxidation two acids (acetic and paratoluic), the formulæ

* The compound $C_{10}H_{18}(OH)(OC_2H_3O)$ was obtained, according to Oppenheim, from terpin.

of which together represent the same amount of carbon as the formula of a molecule of terpinol. The amount of toluic acid produced relatively to the acetic acid is, however, very small, and other substances are formed at the same time.

But the action of sodium and the readiness with which terpinol splits up into water and a hydrocarbon, as well as the action of hydrochloric and sulphuric acids, indicate its character as an alcohol.

The action of sulphuric acid upon terpinol has yet to be described. It is to a certain extent different from that of hydrochloric acid. When heated with it, the result is dehydration, attended by partial polymerisation of the resulting hydrocarbon. This hydrocarbon, called in the preliminary paper terpinylene, is apparently identical with terpilene, an optically inactive liquid obtained by heating the dihydrochloride ($C_{10}H_{18}Cl_2$, m. p. 48°).

But when terpinol is mixed gradually with nearly an equal volume of sulphuric acid, diluted with half its bulk of water, very little heat is evolved, and the liquids do not at first separate. But the acid sulphate which the liquid may be assumed to contain is very unstable, and is completely decomposed by addition of three or four volumes of water, and the whole solidifies in a few minutes into a mass of crystallised terpin, mixed with only a small quantity of liquid hydrocarbon.

Natural Terpinols.

Some of the volatile oils contain ready-formed compounds, which possess the same composition as terpinol, and save for the fact that in some cases they rotate the polarised ray, they differ in no respect from the liquid prepared from terpin. Thus, oil of lemon distilled from fresh lemons contains 10 to 15 per cent. of a liquid which boils at the same temperature as terpinol, and when saturated with hydrochloric acid gas, gives a purple coloration, and finally sets into a mass of crystals of dichloride, which melt at 48°. It differs from common terpinol only in possessing a dextro-rotatory power.

The liquid known as "cajeputol" again, boils at a little above 200°. (The portions which come over at lower temperatures contain hydrocarbons.) It also becomes intensely purple, like terpinol, when exposed to hydrochloric acid gas, and yields a mass of the same dichloride, melting at 48°.

Some rough experiments, made upon fractions of oils of coriander and citronella taken at the same temperature, failed to yield the familiar chloride in crystals, but there was strong coloration and separation of water; and I have very little doubt that these liquids are either identical with terpinol or mere physical modifications of that substance.

Rosin spirit was examined for terpinol, but the fraction separated at 200° to 210° had no smell of terpinol; and although it became coloured by the action of hydrochloric acid, no sign of crystalline chloride could be observed, neither could terpin be produced from it by the action of sulphuric acid.

(*Compare* Mills, "Manualette of Destructive Distillation," p. 33.)

XXXV.—*Researches in Dyeing. Part II. Note on the Emission of Colouring Matter.*

By Edmund J. Mills, D.Sc., F.R.S., and Louis Campbell.

XI. The experiments to which we are about to refer were performed in a manner precisely similar to that described in Part I (*Chem. Soc. J.*, 1879, **1**, p. 26). The colouring matter selected was a sample of Nicholson's blue, well crystallised, and several years old.

Each experimental "vat" contained 0·2780 gram of pure silk ribbon, and 0·0100 gram of Nicholson's blue in 400 c.c. of water. A blank set (A) of five vats was wholly constituted thus: a second set (B) contained, in addition, 1 gram of potassic chloride in each vat; and the third set (C) contained, as its addition, 1 gram of sodic chloride in each vat. The sets and individual vats were marked respectively A_0*, A_1, A_2, A_3, A_4; B_1, B_2, B_3, B_4; C_1, C_2, C_3, C_4. After 24 hours' contact, the silk was withdrawn from A_1, B_1, C_1; after 48 hours, from A_2, B_2, C_2, &c., &c.; and during half of each daily period, temperature observations were made. The residual colouring matter in each vat was determined by means of the portable colorimeter, that which had been left unexhausted in A_0 being regarded as 100. The results are comprised in the following table:—

	A_0.	A_1.	A_2.	A_3.	A_4.
(A.)	100·0	95·6	92·6	87·1	97·6
		B_1.	B_2.	B_3.	B_4.
(B.)	—	78·8	68·7	83·5	99·7
		C_1.	C_2.	C_3.	C_4.
(C.)	—	93·2	78·3	72·4	68·9
Day temp.		11·3°	12·8°	11·7°	11·4°

The extremes of day temperature were 11° and 13°·5.

* This vat contained no silk.

XII. The numerical results in [A] and [B] are not amenable to treatment; those in [C] correspond to an equation—

$$y = 98{\cdot}2(\cdot 912)^x,$$

with a probable error of 1·9 per observation. This probable error is not unduly large, if we bear in mind the method of estimation, and the peculiar difficulties which attend the observation of the tints of the blue substance employed.

XIII. The experiments in [A] and [B] show a very remarkable phenomenon. The energy of combination between the silk and the colouring-matter has been over-developed at first, and the excess of deposit thus taken up has been emitted gradually during the third and fourth days. It is noteworthy that, while this result is well marked in the case of water, it is much more decided when potassic chloride is present, and is wholly prevented by the addition of sodic chloride. A fundamental difference of this kind between these two chlorides is only very rarely encountered. The emission of colouring matter, in some cases, has been previously observed; but we believe our own measurements of it to be the first that have been made.

A solution of 0·009 gram of Nicholson's blue in a litre of water lost much of its colour on boiling, and much more when slowly cooled somewhat below that temperature; a little hydric acetate soon causes the colour to return. The original liquid is instantly bleached by a mere trace of alkali.

XIV. If a solution of the blue be diluted with a considerable amount of water it becomes paler at first, but dark again on long standing. We at one time supposed that we were in fact making measurements of this restored tint in our vats A and B; but the still greater dilution in C, without this restoration occurring at all, convinced us subsequently that we were really dealing with the forcible emission of colouring matter. Moreover, the dilution in our vats proved insufficient to produce any material effect of this kind, though it may possibly have somewhat hampered the colorimetric estimations. In these we were careful to make successive approximations to equality of strength in the comparison tubes, and, as far as could be done, to measure dilutions of equal age.

XV. With regard to the disputed question, whether silk can or cannot be dyed with this peculiar blue, we unhesitatingly express the opinion that a real and uniform dyeing effect is always obtained; this is well seen in our experiments C. The heat and "souring" to which dyers usually have recourse are operations quite apart from the intrinsic deposition of the pigment.

XVI. So far as practical considerations are concerned, we think it advisable not to maintain this blue so long as is usually done at the

dissociation temperature; silk or wool, in such a case, has to work under adverse conditions. Much, also, is to be hoped from the employment of common salt in the vat. It sustains with uniformity the essential dyeing effect, prevents the emission of colour, and thus furnishes a curve without reversal.

XXXVI.—*On the Volumetric Determination of Chromium.*

By W. J. Sell, B.A., F.I.C., Demonstrator of Chemistry in the University of Cambridge.

In the course of some investigations on the sulphates of chromium I discovered that the chromium in ordinary chromic salts, such as chrome alum, might be completely converted into chromic acid by means of potassic permanganate. It occurred to me that this reaction might be made available in the quantitative analysis of compounds containing chromium, more especially the native compound, chrome-iron ore. I think I have succeeded in devising a method by which the amount of this element in chrome-iron ore may be estimated in a much shorter time, and with greater exactitude than the methods in general use.

In attempting the direct estimation a weighed quantity of pure chrome-alum was taken, dissolved in water, acidified with sulphuric acid, heated to boiling, and a decinormal solution of potassic permanganate added from a burette in small quantities at a time, the liquid being allowed to boil freely the whole time. As the end of the reaction was approached, manganese dioxide was precipitated on every occasion, thus necessitating a slightly larger addition of the permanganate than is required by the equation—

$$5Cr_2(SO_4)_3 + 3K_2Mn_2O_8 + 6H_2O = 10CrO_3 + 3K_2SO_4 + 6MnSO_4 + 6H_2SO_4.$$

The direct method was therefore abandoned.

Two other modes were of course yet open.

(1.) To add a known quantity of permanganate, estimate the manganese dioxide, and deduct the value of the latter from the permanganate used.

(2.) To remove the excess of permanganate after neutralisation, by means of alcohol, separate the manganese by filtration, and estimate the chromic acid in solution by any of the ordinary methods.

The latter was the method adopted in these experiments, and gave

results which were all that could be desired in point of accuracy and rapidity of execution.

The following mode of procedure was adopted:—

(1.) 1·874 gram chrome-alum dissolved in water, and the solution diluted to 250 c.c.

Experiment 1. 50 c.c. taken, acidified with 2 c.c. sulphuric acid, heated to boiling-point, and whilst boiling, a dilute solution of potassium permanganate added, in small quantities at a time. The reaction being regarded as complete when the solution retained a distinct purplish tint, after boiling for about three minutes, since the last addition of the permanganate. The solution was rendered slightly alkaline by addition of sodic carbonate, alcohol added, and the manganese removed by filtration, and the chromic acid in the filtrate estimated by iodine and sodic thiosulphate.

Experiment 1 required 20·7 sodic thiosulphate.

Experiment 2, conducted precisely as in Experiment 1, required 20·7 thiosulphate.

Experiment 3, conducted precisely as in Experiment 1, required 20·8 sodic thiosulphate.

Mean of three determinations = 20·73.

Each c.c. thiosulphate = ·01384 iodine.

Amount of chromium found in ·3748 alum = ·03944.

Amount of chromium calculated in ·3748 in alum = ·03931.

(2.) These experiments were mainly directed to determine the possibility of completely converting the chromium into chromic acid, without using an excess of permanganate.

2·700 grams chrome-alum dissolved in water, and the solution diluted to 250 c.c.

Experiment 1.—100 c.c. solution taken and treated as in Series 1, except that the addition of permanganate was discontinued, when the solution acquired a clear bright yellow colour, and the solution diluted to 250 c.c.:—

1.—50 required 11·5 c.c. thiosulphate.

2.—50 „ 11·55 c.c. „

Experiment 2—3. 50 c.c. same solution heated to boiling, and excess of permanganate used as in Series 1.

Experiment 1 required 12 c.c. thiosulphate.

The last result gives for ·216 alum 0·02284 Cr.

Calculation for ·216 alum ·02266 Cr.

From this series of experiments it would appear to be unsafe to stop short of an excess of permanganate.

These preliminary experiments led me to attempt the application of this method to the analysis of the native compound chrome-iron ore. With this object in view ·9665 gram ore was fused in a large platinum

crucible with 8 grams potassium bisulphate, with the usual precautions, and after the crucible had been heated to redness for about half an hour, a further addition of 5 grams of the bisulphate was made to the mass, which after thorough fusion and incorporation was rapidly cooled. The mass was treated with water, which dissolved a large proportion of the chromium, leaving a greenish crystalline residue of a double sulphate of chromium and potassium, which, however, completely dissolved when boiled with a mixture of about equal volumes sulphuric acid and water. The two solutions were mixed and diluted to one litre.

(3.) Experiment 1.—250 c.c. treated as in 1. Experiment 1, the iron, &c., being precipitated with the manganese when a slight excess of sodic carbonate was added, followed by alcohol and filtration, required 41 c.c. sodium thiosulphate.

Experiment 2.—100 c.c. required 16·4 thiosulphate.

These results give 47·09 per cent. Cr_2O_3 in the ore.

Experiment 3.—250 c.c. precipitated by ammonia, the chromium converted into chromate by fusion with sodic carbonate and nitre, the alumina separated, gave ·1137 Cr_2O_3 = 47·06 per cent. Cr_2O_3 in the ore.

(4.) Same sample of ore weighing ·3368 gram treated as in 3, only using less potassium bisulphate, gave complete solution on heating with water, then adding sulphuric acid and boiling. Solution diluted to 250 c.c.

Experiment 1.—50 c.c. treated as in 3 required 11·4 sodic thiosulphate = 46·77 per cent. Cr_2O_3.

(5.) ·316 gram fused with potassic bisulphate, then sodic carbonate and nitre added, as in the usual method for chrome-iron ore, gave ·15 Cr_2O_3, which gives 47·43 per cent. CrO_3 in ore.

In some preliminary experiments I found well-fused sodium bisulphate preferable to the potassium-compound in obtaining a solution of the ore, less time being required for the solution of the sodium salt, and considerably less (in some cases none) of the green double sulphate being formed. On the other hand, like the potassium-compound, it occasionally leaves small quantities of the unaltered mineral on the first treatment.

The following results were obtained by fusing four separate lots of the same sample of ore used in the preceding experiments. The ore was treated in the same manner as in the experiments with potassium bisulphate, the small quantity of undecomposed ore being refused, and the united solutions being diluted to one litre.

(6.) Total weight of ore in one litre = 2·190.

Experiment 1.—50 c.c. treated by new method required 18·6 thiosulphate.

Experiment 2.—50 c.c. treated by new method required 18·6 thiosulphate.

This result gives 47·11 per cent. Cr_2O_3 in ore.

Experiment 3.—250 c.c. solution neutralised with sodium carbonate, the chromium converted into chromate by chlorine in presence of sodic acetate, the iron and alumina separated, excess of sulphurous acid added, and precipitated by ammonia, gave ·2586 Cr_2O_3 = 47·23 per cent.

Experiment 4.—250 c.c. treated as in last experiment, gave ·25797 Cr_2O_3 = 47·11 per cent.

Being still dissatisfied with the large amount of time required for obtaining a suitable solution of the foregoing methods, I tried a modification of the well-known process with hydrofluoride of potassium. After ignition for fifteen minutes with the hydrofluoride, the metal converted into sulphates by the addition of sodium bisulphate, a further quantity of bisulphate being subsequently added, and after thorough fusion and incorporation of the mixture, rapidly cooled. On treating the mass with boiling water, acidulated with a few drops of sulphuric acid, a perfect solution is obtained, the whole operation being performed in less than three-quarters of an hour.

The following method also yielded quite as good results as the last, the whole of the ore being completely acted upon, and yielding a perfect solution in every case, the time occupied being about the same as in the preceding.

A mixture is made of well-fused and powdered sodium bisulphate and sodium fluoride in the proportion of one molecule of the former to two of the latter. This mixture possibly giving the sodium hydrofluoride, thus:—

$$2NaF + NaHSO_4 = NaFHF + Na_2SO_4.$$

The ore is placed on the top of about ten times its weight of the above mixture, and the whole ignited for about fifteen minutes. At the end of this time an amount of sodium bisulphate is added equal to that of mixture taken, and when thoroughly fused and incorporated a further addition of the same quantity of bisulphate is made. A final fusion and incorporation having been obtained, the mass is rapidly cooled and dissolved by boiling with water acidulated with sulphuric acid.

The following further experiments were made with a sample of ore from the same mass as that with which the preceding determinations were made, the solution having been obtained by the method last described:—

·6587 gram of ore was ignited for fifteen minutes with 5 grams of the mixture of sodium bisulphate and fluoride, then two successive

University of Michigan

doses of 4 grams each of sodium bisulphate added, the mixture carefully fused and incorporated after each addition, and the mass boiled with water acidulated with sulphuric acid gave a perfect solution which was diluted to 1 litre.

(7.) Experiment 1.—100 c.c. treated by new method required 11·85 thiosulphate.

Experiment 2.—100 c.c. treated by new method required 11·76 thiosulphate.

Taking the mean as 11·8 c.c., thiosulphate gives for 100 c.c. = ·03274 Cr_2O_3, or for 500 c.c. ·1638 Cr_2O_3 in ·32935 ore.

Experiment 3.—500 c.c. precipitated by ammonia, the chromium converted into chromic acid by a mixture of nitric acid and potassium chlorate, the iron and alumina removed by ammonia, gave, after reduction and precipitation by ammonia with usual precautions,

	Cr_2O_3
	·1641
New method.....	·1638
	·0003 difference.

By using either of the two latter modes for effecting a solution of ore a single determination takes about an hour and a half. It is, however, to be observed that this method may be used successfully with such small quantities of ore as ·1 gram.

My attention within the last few days has been called to a notice by Mr. Wanklyn (in the *Phil. Mag.* for February), in which he states that chromic oxide may be converted into chromate by alkaline permanganate, a result I arrived at some months ago, but have not as yet succeeded in applying quantitatively.

XXXVII.—*On Heptane from* Pinus Sabiniana.

By T. E. Thorpe, Ph.D., F.R.S.

In a paper read to the California Pharmaceutical Society on December 13, 1871, and reprinted in the *Pharmaceutical Journal* for March 30, 1872, Mr. William Wenzell, of San Francisco, describes as new and under the name of *Abietene** a hydrocarbon obtained by distilling the terebinthinate exudation of a coniferous tree, *Pinus sabiniana, Dougl.* This tree is indigenous to California, and grows on the dry slopes of the foot-hills of the Sierra Nevada and on the hills along the

* The name *Abietin* was originally applied by Caillot to a resin obtained from the turpentine of *Abies picea* and *Abies balsamea.*

coast; it appears to be pretty plentiful, and is known locally as the nut pine or Digger pine, names suggested by the circumstance that the Digger Indians rely to some extent on its fruit for food.

In order to procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil is met with in San Francisco as an article of commerce, and during the last few years has acquired some reputation under the names of "abietene," "erasine," "aurantine," "theoline," &c., as a substitute for "benzoline" or "petroleum benzene" for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless mobile liquid of powerful aromatic smell, recalling that of oil of oranges. The crude oil, according to Mr. Wenzell, boils almost entirely between 100° and 105°, and on redistillation the liquid is obtained of the constant boiling point of 101°. The portion boiling above 105° leaves on evaporation a small quantity of a resinoïd body possessing the strong penetrating odour of the original product. The liquid is highly inflammable and burns with a brilliant white smokeless flame. Its vapour is powerfully anæsthetic, and it has been used with success as an insecticide.

No analysis or vapour-density determination of this liquid is given in the communication above referred to, nor does Mr. Wenzell offer any opinion as to its real nature. He contrasts its characters with those of terebene (spirits of turpentine), the hydrocarbon obtained from *Pinus palustris*, *P. sylvestris*, &c., and points out the very striking differences observed in their physical and chemical properties. Abietene has a specific gravity of 0·694 at 16·5°, whilst that of terebene is 0·840 at about the same temperature. Oil of turpentine boils at 160°, whilst the boiling point of abietene is 101°. Hydrochloric acid gas is but slightly dissolved by abietene, whereas oil of turpentine absorbs it with avidity. Nitric acid acts violently on oil of turpentine; it has little or no action on abietene in the cold.

Abietene was evidently sufficiently remarkable to merit further investigation. From its general behaviour towards reagents, it seemed not unlikely that it would prove to be a paraffin, and the boiling point and specific gravity appeared to indicate *normal heptane*. The occurrence of heptane, or indeed of any other paraffin, playing the part of oil of turpentine in the vegetable kingdom was hitherto unheard of. The only natural source of this hydrocarbon was petroleum or some of the fossil-fish oils obtained in Greenland, Switzerland, and other places. Menhaden oil contains considerable quantities of heptane, and it is met with among the products of the destructive distillation of cannel and shale.

Through the kindness of Mr. H. B. Brady, F.R.S., I was able to obtain, through Dr. Squibb, of New York, about a couple of gallons

of abietene from Mr. Wenzell. The crude oil fully answered the description already given of it by the latter gentleman. It was almost colourless, and had the strong persistent odour of oil of oranges. It began to boil slightly below 100°, and the greater part distilled below 101°. The residual portion darkened slightly, and on evaporation left a small quantity of resinoïd matter of a brown colour, which had the peculiar smell of the liquid in a very high degree. This led to the supposition that the odour of the crude oil might be due in great part to the resin in solution, and further examination proved this to be the case. On agitating it for some time with oil of vitriol the acid became brown, and on again distilling the hydrocarbon was found to have lost its smell of orange oil.

Two determinations of its boiling point were made by the aid of a thermometer capable of being read to 0·01° C. The first observation gave 98·27° at 755·6 mm., the second 97·93° at 746·9 mm. The mercurial columns in both cases were wholly immersed in the vapour, and the barometric pressures are corrected and reduced to 0° C. Assuming the validity of the well-known expression—

$$T = t + 0{\cdot}0375(b - 760),$$

where t is the observed boiling point and b the barometric pressure, the boiling point, T, under the standard pressure becomes respectively—

I ..... 98·43°
II ..... 98·42

The first determination was made on about three litres of the liquid, the second on about 250 c.c., after a second treatment with a mixture of nitric and sulphuric acids; in both cases the liquid boiled as constantly as distilled water. In all I obtained about seven litres of the perfectly pure substance from seven and a half litres of the crude oil.

That abietene is actually heptane is proved by the following analyses and determinations of vapour-density :—

I. 0·3500 gram hydrocarbon gave 1·0754 gram CO_2 and 0·5050 gram H_2O.

II. 0·3000 gram hydrocarbon gave 0·9215 gram CO_2 and 0·4336 H_2O.

	Calculated for C_7H_{16}.	Found. I.	II.
C	83·97	83·85	83·78
H	16·03	16·03	16·06
	100·00	99·88	99·84

Two determinations of its vapour-density, made in a modified form of Hofmann's apparatus,* gave the following results:—

I.	Weight of liquid	144·5 mgm.
	Volume of vapour (corrected for expansion of glass, error of meniscus, &c.. ..	90·39 c.c.
	Temperature of vapour.....	99·90° C.
	Barometer (corrected and reduced)....	757·6 mm.
	Height of mercury in tube (reduced)..	387·8 „
II.	Weight of liquid.....	76·9 mgm.
	Volume of vapour (corrected)	69·77 cc.
	Temperature	99·60° C.
	Barometer	749·0 mm.
	Height of mercury in tube	493·4 „

Calculated for C_7H_{16}.	Found. I.	II.
49·90	50·07	49·94

I. *The Physical Characters of Heptane from Pinus Sabiniana.*

The possession of so large a quantity of perfectly pure heptane has induced me to study some of the physical characters of this hydrocarbon. These observations have included the determination of its specific gravity, and the measurement of its thermal expansion, refractive index, optical activity, viscosity, and superficial tension.

Specific Gravity.—Three determinations of specific gravity made with different bottles gave the following results:—

0·68848 at 14·98°
0·68855 „ 14·87
0·68858 „ 14·87

compared with water at the same temperatures respectively. The weighings were made by the method of vibrations and the weights are reduced to a vacuum. Reducing these results by the aid of Rossetti's tables for the expansion of water, and by means of the formula for the thermal expansion of heptane given below, the specific gravity at 0°, compared with water at 0°, becomes respectively—

0·70057
0·70055
0·70058

Mean .. 0·70057

* The apparatus here referred to allows of the determination of a vapour-density with almost as much exactitude as that of any other physical constant; it was designed more especially with a view of controlling the purity of some liquids employed in a research involving the determination of a number of thermal expansions.

Thermal Expansion.—The rate of expansion of the heptane was determined by heating the hydrocarbon in dilatometers properly calibrated and graduated. The volume of the hydrocarbon at 0° was obtained by immersing the dilatometers in melting snow. The instruments were then placed in a large copper bath fitted with plate-glass sides, and holding several litres of water which could be kept in constant motion by stirrers worked by a small hydraulic engine. The water was heated by steam and the temperature ascertained by thermometers capable of being read to 0·01° C.

Two series of observations were made. The first set gave the following results:—

Temperature.*	Observed volume.	Calculated volume.	Temperature.	Observed volume.	Calculated volume.
0·00	3290·1	3290·4	53·71	3516·3	3516·9
9·04	3326·1	3326·0	62·80	3560·1	3559·9
17·27	3359·2	3359·1	72·12	3606·2	3605·7
26·96	3398·9	3399·1	80·68	3649·5	3649·5
35·55	3435·9	3435·7	87·32	3684·2	3684·6
44·96	3477·2	3477·1	93·70	3719·9	3719·4

Combining the results by the method of equation of conditions we obtain the formula—

$$3290{\cdot}361 + 3{\cdot}895352t + 0{\cdot}00432087t^2 + 0{\cdot}00003183t^3,$$

by means of which the numbers in the third column of the above table are calculated.

The second series made in a different dilatometer gave the following data:—

Temperature.	Observed volume.	Calculated volume.	Temperature.	Observed volume.	Calculated volume.
0·00	2879·6	2879·3	53·71	3076·4	3077·0
9·04	2910·5	2910·6	62·81	3114·5	3114·5
17·27	2939·3	2939·5	72·13	3155·2	3154·7
26·97	2974·2	2974·5	80·68	3193·6	3193·2
35·54	3006·4	3006·2	87·27	3223·8	3224·1
44·96	3042·3	3042·3	93·71	3255·3	3255·4

* These temperatures are expressed in degrees of the air thermometer in order to make them uniform with my other observations of thermal expansion. The conversion from the ordinary thermometric values is effected by a table compiled from Regnault's and Recknagel's comparisons of the air and mercurial thermometers (see Wullner's *Lehrbuch der Physik*). To convert the degrees of the air thermometer into those of the mercurial thermometer *add* 0·08° at 10°, 0·16° at 25°, 0·16° at 65°, 0·1 at 80°.

These numbers afford the expression—

$$2879{\cdot}302 + 3{\cdot}432882t + 0{\cdot}00247831t^2 + 0{\cdot}00003964t^3,$$

by the aid of which the numbers in the third column of the above table are computed.

Dividing through by the first terms respectively and correcting for the expansion of the glass of the dilatometers (0·00002130 for 1° in Series I, and 0·00002303 in Series II) the formulæ become—

$$\text{I. } 1 + 0{\cdot}00120517t + 0{\cdot}00000133841t^2 + 0{\cdot}000000009701t^3.$$

and

$$\text{II. } 1 + 0{\cdot}00121529t + 0{\cdot}00000088819t^2 + 0{\cdot}000000013787t^3.$$

The mean formula is—

$$1 + 0{\cdot}00121023t + 0{\cdot}0000011133t^2 + 0{\cdot}00000001174t^3,$$

by the aid of which the following table showing the relative volumes of heptane from *Pinus sabiniana* at every 5° between 0° and 100° is calculated:—

Temperature.	Volume.	Difference.	Temperature.	Volume.	Difference.
0	100000	—	55	107188	712
5	100608	608	60	107916	728
10	101222	614	65	108659	743
15	101844	622	70	109420	761
20	102474	630	75	110198	778
25	103114	640	80	110995	797
30	103763	649	85	111812	817
35	104423	660	90	112650	838
40	105094	671	95	113509	859
45	105778	684	100	114390	881
50	106476	698			

The volume at the boiling point 98·43° is 1·14111: hence the specific gravity at this temperature is 0·61393, which gives for heptane *the specific volume* 162·54. Kopp's values (C = 11; H = 5·5) afford the number 165.

Refractive Index.—A careful set of observations of the index of refraction of heptane from *Pinus sabiniana* was made for me by Mr. John I. Watts in the Physical Laboratory of the Owens College by one of Elliott's horizontal goniometers.

Five concordant determinations of the angle of the prism employed gave as a mean result—

$$\theta = 59° 12' 20''.$$

The same number of observations of the angle of minimum deviation gave—

$$\delta = 27° 21' 44''.$$

The source of light was a sodium flame. The temperature of the liquid was 17·6°.

Inserting these numbers in the well-known formula—

$$\mu = \frac{\text{sin. } \frac{1}{2}(\delta + \theta)}{\text{sin. } \frac{1}{2}\theta}.$$

we obtain 1·3879 as the refractive index for D.

The *specific refractive energy*, $\frac{\mu - 1}{d}$, where d is the specific gravity of the liquid at 17·6°, is 0·565; whence the *molecular refractive energy* is 56·4, in close accordance with the computed number 55·8, calculated by Landolt's values, C = 5, H = 1·3.

Optical Activity.—It is well known that the various terpenes are optically active, often to a very remarkable extent: hence a special interest seemed to be attached to the question of the behaviour of the heptane of *P. sabiniana* towards polarised light. Through the kindness of Professor Gamgee, Mr. J. H. Poynting was able to make a number of observations on the hydrocarbon by means of an excellent Laurent's polarimeter belonging to the Physiological Laboratory of the Owens College. These observations seem to indicate that the heptane does actually rotate the plane of the polarised ray, although to a very slight extent only, a column 200 mm. long exhibiting a rotatory power of + 6·9′. This amount is so small, that I was disposed to attribute it to the possible presence of impurities, despite the careful rectification to which the hydrocarbon had been subjected: the original exudation might have contained small quantities of a terpene, or a minute trace of the resinous matter which it has been stated the crude oil leaves on evaporation might still be contained in the distilled hydrocarbon. The liquid with which Mr. Poynting experimented was accordingly agitated with a mixture of concentrated nitric and sulphuric acids at frequent intervals for several days, but the acids remained perfectly colourless, and the hydrocarbon after redistillation showed precisely the same rotatory power as before, viz., + 6·9′. I am inclined to believe, however, that an optically active terpene is actually present in crude abietene, although not to a greater extent than 0·5 per cent.: the liquid residue left on distilling the crude oil boiled between 140° and 160°, and showed a rotatory power of −12° 23·5′: this liquid, it should be noted, had not been treated with acids. The resin itself, in alcoholic solution, appears to be optically inactive.

Viscosity.—The capillary transpiration of the heptane from *Pinus sabiniana* was determined by a method identical in principle with

that already employed by Poiseuille, Graham, and others; this consists in noting the time required for a given volume of the liquid at some particular temperature and under a uniform pressure to flow through a cylindrical capillary tube of known dimensions. The capillary tube employed was 85·4 mm. in length and 0·2105 mm. in internal diameter: it was sealed, at right angles, to a long cylindrical bulb, containing between two marks etched on the narrow tube above and below the bulb 14·7755 c.c. The open end of the capillary tube was connected with a receiver and the whole was so arranged that it could be immersed in a large bath fitted with plate-glass sides and holding several gallons of water. The temperature of the bath, and therefore of the hydrocarbon contained in the bulb and tubes, could be raised to any desired point below about 80° by heating a coil of copper tube affixed to the side of the bath through which the water from the bath continually circulated. The liquid in the bath was kept in constant agitation by means of stirrers worked by a small hydraulic engine; and the temperature was ascertained by a thermometer capable of being read to 0·01° C. The hydrocarbon was drawn into the bulb by the aid of the air-pump, and as soon as it had acquired the temperature of the bath, it was forced through the capillary tube by the pressure of a confined volume of air kept at a nearly constant tension of 111·2 mm. of mercury by the weight of a column of water of uniform height; and the times at which the level of the liquid passed the two marks, as observed through a telescope, were noted on a chronometer. This apparatus has been employed by Mr. John Muir, student in the Laboratory of the Yorkshire College, in the determination of the viscosity coefficients of a number of liquids; a detailed description of it is reserved for a communication containing the results of his experiments.

Two independent series of observations were made with heptane with the following results:—

Series I.

Temperature.	Time (seconds).	V.	η.	Temperature.	Time (seconds).	V.	η.
6·72°	931·7	7313	·005268	35·07°	611·1	11151	·003454
10·27	794·3	8579	·004490	40·16	582·2	11704	·003292
15·31	749·3	9094	·004236	44·75	560·4	12159	·003168
20·05	710·9	9585	·004019	49·70	534·7	12745	·003023
25·06	673·8	10113	·003810	54·84	512·0	13309	·002895
29·95	642·9	10599	·003635				

Series II.

Temperature.	Time (seconds).	V.	η.	Temperature.	Time (seconds).	V.	η.
7·09°	845·0	8064	·004777	30·06°	639·6	10654	·003616
10·31	792·9	8594	·004482	35·03	611·6	11141	·003457
15·30	749·3	9094	·004236	39·16	585·2	11645	·003300
20·15	713·0	9557	·004031	45·37	555·7	12262	·003142
25·09	673·6	10116	·003808	49·30	538·0	12666	·003042

The transpiration times are corrected for any slight irregularities in the pressure (these never exceeded 0·4 mm. of mercury), and for the change in the dimensions of the bulb and capillary tube by heat.

If Q be the volume of the liquid flowing through the tube in the time t, p the pressure under which it is driven expressed in millimetres of water, l the length of the tube, and r its radius in millimetres, then the volume, V, in cubic millimetres flowing in one second of time through a tube 1 mm. long, 1 mm. radius, and under a pressure of 1 mm. of water, on the assumption that Poiseuille's laws hold good under these conditions, is given by the formula—

$$V = \frac{Q \cdot l}{t \cdot p \cdot r^4}.$$

The numbers so obtained are given in the third column of the above tables.

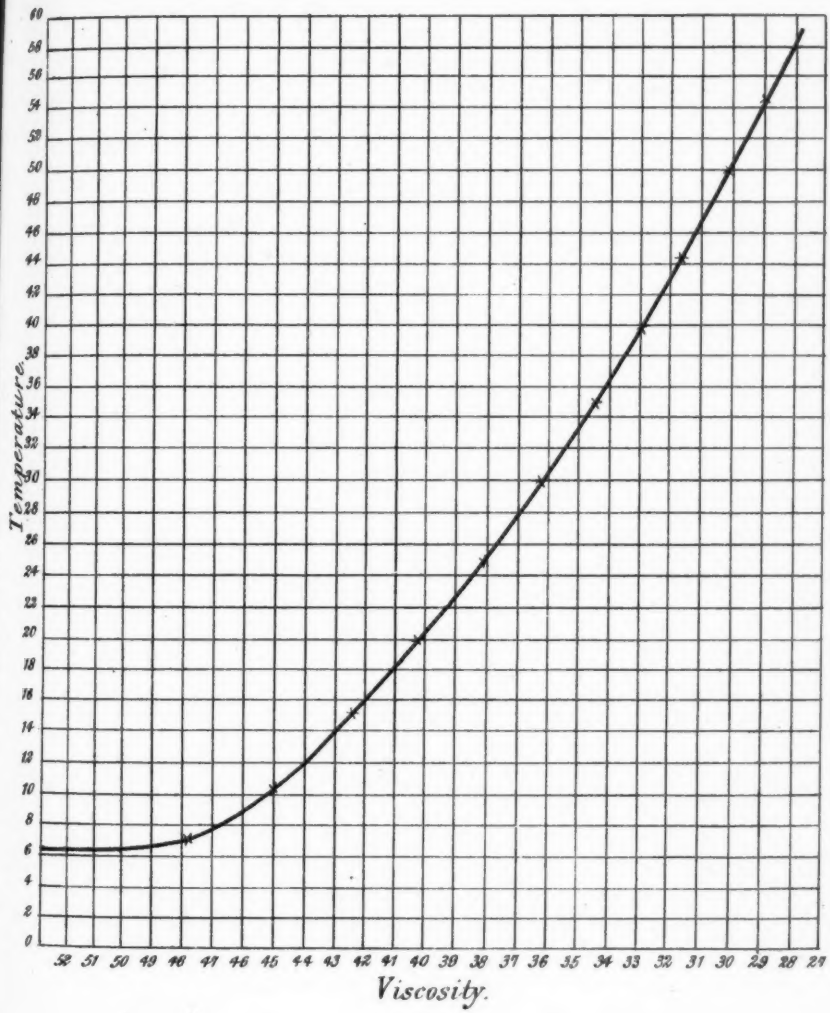
If all the particles of the moving liquid are flowing in parallel straight lines, with velocities proportional to their distances from a plane parallel to these lines, then of any two contiguous layers, the motion of that which moves the more rapidly will be retarded by a force (viscosity) dependent, *cæteris paribus*, on the nature of the liquid, and varying with its temperature. The coefficient of viscosity in absolute measure is the force expressed in dynes thus exerted on a liquid surface one square centimetre in area, lying in a plane of uniform velocity, when the difference of the velocities of two layers one centimetre apart is one centimetre per second.

The viscosity coefficients, η, of heptane for the particular temperatures given in the table, are directly obtained from the values of V in absolute measure by the expression—

$$\eta = \frac{\pi \cdot 98{\cdot}1}{8 \cdot V},$$

by means of which the numbers in the last columns of the above tables are calculated. These results are graphically represented in the accompanying figure.

It will be noticed that the viscosity suddenly diminishes at some



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point between 8° and 10°. After the latter temperature has been reached the rate of diminution is very regular, and may be represented by an expression of the form—

$$\eta = a + bt + ct^2.$$

Combining all the observations in both series of experiments made at temperatures above 15° by the method of equation of conditions, we obtain the formula—

$$\eta = 0{\cdot}005003 - 0{\cdot}00005501t + 0{\cdot}0000003061t^2,$$

which gives results in close accordance with the observed mean values, as the following comparison between the experimental and computed values shows:—

$t°$.	η.		Difference.	$t°$.	η.		Difference.
	Observed.	Calculated.			Observed.	Calculated.	
15·31	·004236	·004233	·000003	39·66	·003300	·003303	·000003
30·10	·004025	·004021	·000004	45·06	·003155	·003145	·000010
25·07	·003809	·003816	·000007	49·50	·003032	·003031	·000001
30·01	·003625	·003628	·000003	54·84	·002895	·002907	·000012
35·05	·003456	·003451	·000005	98·43	—	·002554	—

Surface Tension.—The superficial tension of the heptane from *P. sabiniana* was determined (1) by observations on the rise of the hydrocarbon in a cylindrical capillary tube of known diameter, and (2) by measurements of the form of an air-bubble placed under a plate of glass held under and parallel to the surface of the liquid.

In the first series of observations the apparatus was so arranged that the relation of the surface tension to the temperature could be ascertained from observations on the rise of the liquid in the same tube at different temperatures. A detailed description of the apparatus is reserved for a communication giving the results of an extended series of observations on the surface tension of liquids with special reference to their chemical relations. The measurements were made by the aid of a cathetometer belonging to my colleague, Professor Rücker, and reading to 0·02 mm., and each result is the mean of some six or eight observations. Diameter of tube 0·2531 mm.

Temperature.	Height from the outside level of the liquid to the lowest point of the meniscus in the capillary tube. Observed.	Calculated.	Difference.
7·0	49·62 mm.	49·76	+0·14
15·6	48·36	48·20	−0·16
23·8	46·70	46·71	+0·01
30·2	45·58	45·54	−0·04
38·4	43·99	44·05	+0·06
45·5	42·72	42·76	+0·04
54·6	41·12	41·11	−0·01
60·4	40·10	40·05	−0·05
69·5	38·44	38·39	−0·05
76·8	36·99	47·07	+0·08

No correction has been made for the increase in the diameter of the tube with the temperature. The correction for a difference of temperature of 100° would not affect the fourth place of decimals in the value of the diameter. Combining the observations by the method of least squares, we find that the height of the liquid in the capillary tube may be accurately represented by the expression—

$$h = 58{\cdot}032 - 0{\cdot}1818t.$$

The values calculated by this formula are given in the third column of the above table.

The above formula for a tube 1 mm. in radius becomes—

$$\mathrm{H} = 6{\cdot}4581 - 0{\cdot}0230067t.$$

If the constant of capillarity (a) be considered as half the weight in milligrams of a column of liquid, of which the area of the base is 1 square millimetre, and of which the height is that of a column of liquid in a tube 1 mm. radius, then—

$$a = \frac{\mathrm{H} \cdot s}{2},$$

in which s is the specific gravity of the liquid. This for heptane at 0° is—

$$a = \frac{6{\cdot}4581 \times 0{\cdot}70057}{2} = 2{\cdot}2621 \text{ mgm.}$$

Neglecting the angle of capillarity, which, as the observations with the air-bubble show is certainly not very far from 180°, the surface tension in C. G. S. units at 0° is—

$$\mathrm{T} = 2{\cdot}2621 \times 9{\cdot}81 = 22{\cdot}19,$$

and its relation to the temperature is expressed by—

$$T = 22{\cdot}19(1 - 0{\cdot}003563t).$$

The observations with the air-bubble were made practically in the manner described by Quincke (*Pogg. Ann.*, **139**, 1). A rectangular trough $2\frac{1}{2}$ inches broad, 3 inches long, and 1 inch deep, made of plane parallel plates of glass, cemented together at the edges, was levelled before the cathetometer and filled with the heptane, and another plate of glass was then immersed in the liquid to a depth of a few millimetres, and carefully adjusted until it was parallel with the surface. A bubble of air about 30 mm. in diameter was then blown under the glass by means of a bent capillary tube, and its depth (K), together with that of the point where its tangent plane was vertical (k), was determined by the cathetometer.

The value of the superficial tension in C. G. S. units is given by the expression—

$$T = \tfrac{1}{2}(K - k)^2 gs.$$

In the first set of observations ten readings of K and k were taken. The temperature was 15°.

$K = 3{\cdot}622$ mm. $\qquad k = 1{\cdot}083$

$g = 9{\cdot}81$ $\qquad s$ at 15° $= 0{\cdot}6882$.

Hence $T = 21{\cdot}80$.

In the second set five readings of K and k were taken on another bubble. The temperature was 10°.

$K = 3{\cdot}452$ mm. $\qquad k = 0{\cdot}960$. $\qquad s = 0{\cdot}6922$.

Hence $T = 21{\cdot}12$.

These numbers agree very well with those deduced from the height of the liquid in the capillary tube.

The method of measurement was scarcely accurate enough to afford any very reliable value of the angle of capillarity. This is given by the formula—

$$\text{Cos. } \theta = \frac{K^2}{(K - k)^2} - 1.$$

Combining all the observations, we find the angle of capillarity of heptane 167°. It is worthy of note that the heptane from *Pinus sabiniana* has the lowest surface tension of any liquid yet measured.

Since the superficial tension of a liquid entirely vanishes at the critical point, that is at the temperature at which the gaseous and liquid states become continuous, the expression $1 - {\cdot}003563t$ may afford us an approximation to the critical point of heptane, if we assume that the rate of diminution in capillarity is represented by this

formula at high temperatures. We thus find the critical point of the heptane to be 281°.

Whether the heptane from *Pinus sabiniana* is absolutely identical with that boiling at about the same temperature obtained from petroleum and shale oil remains to be established. The existing evidence, so far as it goes, seems to indicate that the hydrocarbons are really isomeric.

In May, 1874, Professor Schorlemmer, to whom I am indebted for a number of organic preparations for determination of certain of their physical constants, kindly sent me a quantity of normal heptane from petroleum, which he believed to be practically free from the isomeride boiling at 90°, and from octane. I found it to boil constantly between 98·1° and 99·1° under a pressure of 765 mm. Its specific gravity at 0° compared with water at 4° was 0·7299.

In May, 1877, Professor Schorlemmer sent me a second sample of petroleum heptane which had been prepared with special care. This I found to boil between 98·1° and 98·6° under a barometric pressure of 750·3 mm.

A determination of its vapour-density afforded the following data:—

Weight of hydrocarbon.....	150·7 mgm.
Volume of vapour	91·28 c.c.
Temperature	99·8° C.
Pressure	381·3 mm.

Calculated.	Observed.
49·9	50·1

Two determinations of its specific gravity at 0° compared with water at 4° gave—

I	0·7301
II	0·7301

numbers which are almost identical with that afforded by the first sample, and much higher than that of the heptane from *P. sabiniana*, viz., 0·70057.

On the other hand, the hydrocarbon from *P. sabiniana* has precisely the same specific gravity as that of the heptane obtained by heating azelaic acid with caustic baryta. Dale found that the latter body boils at 98—99°, and has a specific gravity of 0·6851 at 17·5°; Schorlemmer, who procured the same hydrocarbon in larger quantity, observed 0·6840 at 20·5°. Reducing these observations by means of the formula given on page 301, they become respectively—

I	0·6992
II	0·7000

If, as Schorlemmer believes, the heptanes from azelaic acid and petroleum are probably identical, the difference in their specific gravities is at present inexplicable. We are now engaged on a joint investigation on the chemical constitution of the heptane from *P. sabiniana*, which may incidentally throw light on this question.

XXXVIII.—*Preliminary Note on certain Compounds of Naphthalene and Benzene with Antimony Trichloride, &c.*

By Watson Smith.

In the course of my investigations on the action of antimony trichloride and tin tetrachloride on naphthalene and benzene at high temperatures, I have obtained crystalline compounds, in some cases apparently of mere molecular constitution, in others in which hydrochloric acid has been evolved, and substitution has taken place, and finally, in the case of antimony and naphthalene, a compound in which chlorine is no more present. The antimony compounds referred to were obtained as follows:—On one occasion in distilling a mixture of antimony trichloride and naphthalene through a red-hot tube with the object of preparing dinaphthyl, this mixture which had already been passed through once or twice, was found to contain a little water accidentally admitted. The gas-pressure chanced also at the time to be low, the heat being only a dull red. It was observed that more hydrochloric acid than usual was evolved, especially considering the low temperature of the tube, and this fact caused me to persevere with the experiment, despite the presence of the water and the unpleasant bumping of the distillation flask. When the contents of the flask had passed through the hot tube, the latter was cleared by means of a long wire of all carbon adhering to the interior, but on this occasion instead of carbon, beautiful long white needles with a diamond lustre fell from the tube. These needles were qualitatively examined as follows:—A portion was boiled with fuming nitric acid, the whole evaporated carefully to dryness, and the residue warmed with tartaric acid, filtered, and hydrogen sulphide passed through the filtrate. The orange precipitate obtained sufficiently proved the presence of antimony in the needles. Another portion was heated in a bent tube with excess of pure powdered cupric oxide, and the evolved gas was passed into lime-water, which it at once rendered milky, indicating that the body is a carbon-compound. A third portion was gently ignited with metallic sodium, and the residue was warmed with water. The whole

being filtered, a few drops of nitric acid, and then silver nitrate, were added to the filtrate. Non-formation of a precipitate or even cloud shows that no chlorine is present in the substance. The crystals when heated on platinum foil melted at a very high temperature, a red heat in fact, then burnt with flame, and entirely disappeared, but the platinum-foil was found just at this part eaten into small holes by the antimony. The crystals are insoluble in water, and unacted upon by it, cold or hot. They are also insoluble in alcohol, ether, carbon bisulphide, benzene, and petroleum ether.

The body I believe will very possibly turn out to be either trinaphthyl stibene, $Sb(C_{10}H_7)_3$, or naphthyl oxystibene, $SbO.C_{10}H_7$, formed respectively, most probably, as follows:—

$$Sb\begin{cases} Cl,H & OH,H & -C_{10}H_7 \\ Cl,H & OH,H & -C_{10}H_7 \\ Cl,H & OH,H & -C_{10}H_7 \end{cases} \quad \text{or} \quad Sb\begin{cases} Cl,H & -C_{10}H_7 \\ Cl_2H_2 & =O \end{cases}$$

$$SbCl_3 + 3H_2O + 3C_{10}H_8. \qquad SbCl_3 + H_2O + C_{10}H_8.$$

I have not been successful in the one trial I have so far made to repeat the experiment, and to obtain a further yield of this new compound. A mixture of fresh antimony trichloride and naphthalene was taken in this attempt, and to this a few drops of water were added, and the distillation was conducted as nearly as possible under the same conditions as before, but without avail. It now seems more probable that some compound is first formed in the red-hot tube, which is subsequently decomposed in passing through the tube a second time in presence of steam. I shall, therefore, in my next attempt first pass the mixture through the red-hot tube once or twice, and then add the water, and distil once more through. The other compounds were discovered on purifying the crude black product containing dinaphthyl by distillation, to separate naphthalene and antimony trichloride. It was observed that when the distillate, which passed over between 212° and 230°, was kept separately and left to cool, it yielded on the surface beautiful transparent clino-rhombic tables, which on standing for a short time became opaque and almost white, and then exhibited a mother-of-pearl lustre and play of colour. These crystals are deliquescent and easily decomposed by water and alcohol, and appear also to be decomposed by benzene on solution therein, with formation of a benzene compound of antimony chloride. On melting together a simple mixture of naphthalene and antimony trichloride, and leaving it to cool, I readily obtained the clino-rhombic crystals of this body. Returning to the distillation, it was now observed that the distillate passing over between 230° and 270° possessed a red tinge, the latter portions being quite crimson. The red colour for the most part faded

on cooling, and fine prismatic needles, consisting apparently of long clino-rhombic prisms with pyramidal apices, crystallised out. These crystals are not nearly so deliquescent as the foregoing, nor so easily decomposed by water and alcohol. A certain amount of hydrochloric acid gas was evolved as this distillate passed over, and the fused mass before crystallising smelt of hydrochloric acid. The body crystallises apparently unaltered from petroleum ether, in long lanceolate needles.

I have obtained crystalline compounds, too, by the action of antimony trichloride on benzene, and likewise by the action of tin tetrachloride on both naphthalene and benzene, which I have not yet more minutely examined. It seems to me now very probable that by the action of the antimony potassium alloy (SbK_3) on bromonaphthalene or bromobenzene at high temperatures, trinaphthyl stibene and triphenyl stibene should be obtained. These interesting points I hope shortly to settle. Gustavson has recently obtained molecular compounds of benzene and aluminium chloride decomposible by water, and violently by bromine, with formation of perbromobenzene. It will be interesting to observe the action of bromine on the molecular compounds I have in all probability obtained, of antimony trichloride and naphthalene, and also benzene. Some of the practical results of these inquiries I hope soon to lay before this Society.

XXXIX.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. 1.—*On conditions affecting the Equilibrium of certain Chemical Systems.*

By M. M. Pattison Muir, Caius Prælector in Chemistry.

It is well known that a given chemical system is capable of assuming more than one stable configuration, each configuration being conditioned by certain physical circumstances. Temperature, time, mass, &c., &c., all exert a more or less marked influence upon the chemical distribution, at any moment, of the masses of matter which comprise a given system.

When all the members of such a system are free to act and react, the influence of extraneous physical forces upon the stability of the system is very marked (see Gladstone, this Journal, **9**, 54; Harcourt, *ibid.*, **20**, 460; Lemoine, *ibid.*, 1877, ii, 828, &c., &c.).

But even in cases where one, or more of the compounds produced during the change from one configuration to another is partially removed from the sphere of action, we find that the points of maximum stability vary with variations in physical conditions.

If one of the products of the change be gaseous, and if the change be allowed to proceed in an enclosed space, a series of states of stable equilibrium is attained, each marked by a different tension of the gaseous product of the change. The conversion of phosphorus α into phosphorus β, and the oxidation of phosphorus, in pure oxygen, only under diminished pressure, are cases in point.

If each chemical system be characterised, as it undoubtedly is, by the possession of a definite amount of energy, then any force which tends to alter that energy will also tend to disturb the chemical equilibrium of the system.

Such forces are time, temperature, mass, concentration, nature of the containing vessel, &c., &c. If any, or several, of these conditions be largely exaggerated, abnormal results may be obtained. Thus Troost and Hautefeuille (this Journal, 1877, ii, 273) state that if oxygen be submitted to the action of the silent discharge at a temperature of 1300°, while the outer portions of the oxygen are cooled to a moderate temperature, ozone is produced.

If the passage from one configuration to another be attended with a loss of energy, that passage usually occurs. Thus Berthelot (this Journal, **34**, 108) shows that dry BaO_2 is stable, while moist BaO_2 slowly changes to BaH_2O_2; now the change $BaO_2 = BaO + O$ would involve an absorption of about six units of heat, but the change $BaO_2 + H_2O = BaH_2O_2 + O$ is accompanied by the evolution of nearly three units of heat.

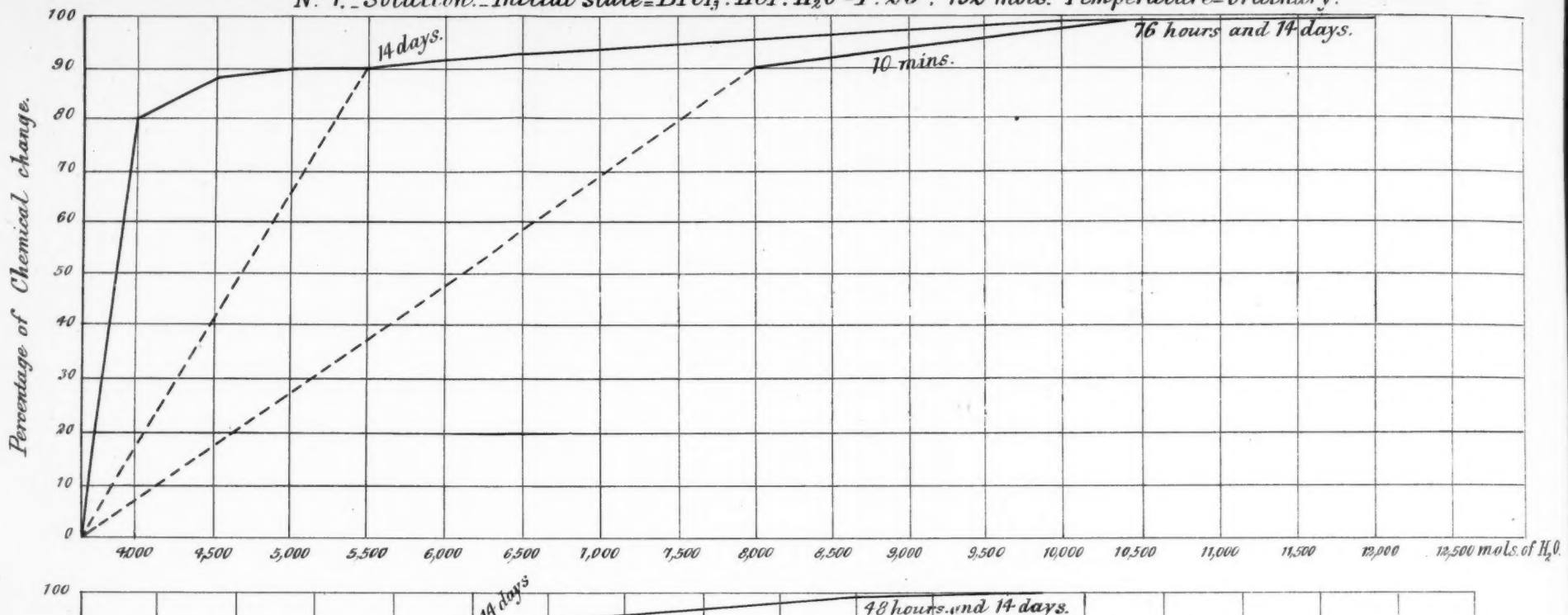
If the view be adopted that in a chemical system which is in stable equilibrium, atomic interchanges are constantly occurring to a greater or less extent, and that so long as the molecular decompositions and recompositions are equal in unit of time, the configuration remains stable, but that any action which tends to increase the former without directly influencing the latter, tends to disturb the equilibrium, then I think we are presented with a fairly workable hypothesis to guide us in our examination of the conditions which influence chemical equilibrium.

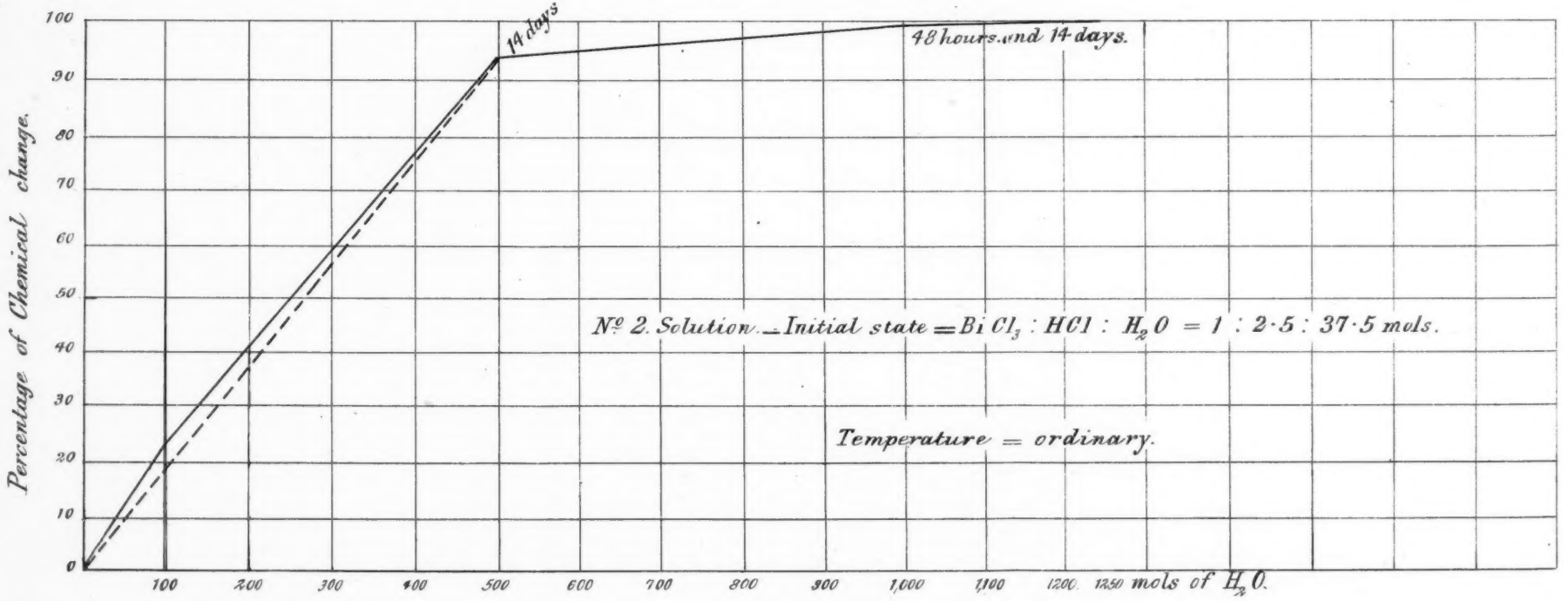
It is the object of the present paper to examine in some detail the conditions which affect two cases of chemical equilibrium, with the view of arriving at general results concerning these conditions, and, if possible, of throwing some light upon the general conditions affecting the equilibrium of such chemical changes as result in the production of comparatively insoluble compounds.

1. The action formulated $BiCl_3 + xH_2O = BiOCl + 2HCl +$

TABLE A. *(For numerical details see Tables I to IV.)*

INFLUENCE OF MASS.





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zH_2O, presents us with a chemical change, the investigation of which seemed likely to throw light upon the subject of chemical equilibrium. The products of this change, viz., hydrochloric acid and bismuthyl chloride, are not without chemical action upon each other: the change is one which admits of tolerably accurate measurement without the introduction of a foreign body, the entrance of which might disturb the equilibrium of the reacting system.

2. Solutions of pure bismuthous oxide in hydrochloric acid (containing known amounts of the acid and water) were prepared, and the proportion between bismuthous chloride, hydrochloric acid, and water molecules in each solution was calculated. A measured volume of each liquid was placed in a suitable vessel, and a quantity of water, representing a determinate number of molecules, was run in from a measuring vessel. The liquid was thoroughly shaken, and then allowed to remain at rest for a fixed number of minutes, hours, or days. At the expiry of the proper time, the whole or a portion of the clear supernatant liquid was withdrawn, run through a dry filter if necessary, and the amount of bismuth remaining in solution was determined in an aliquot portion of this liquid. Many of the experiments were made in duplicate.

From the results obtained the proportion of bismuthous chloride which had been converted into oxychloride was calculated.

3. The following tables, I to IV, comprise the more important numerical results, as these bear upon the question of the disturbing influence of mass of water and of bismuthous chloride.

TABLE I.—*Influence of mass.* (Compare curves of Table A.)

13·816 grams Bi_2O_3 dissolved in 239 c.c. aqueous HCl (1 c.c. = 0·2701 gram HCl and 0·8519 gram H_2O) and 1·8 c.c. H_2O added.

After solution have	18·687 grams $BiCl_3$.	Solution No. 1.
	58·095 „ HCl.	
	207·852 „ H_2O.	

or in molecular proportion, $BiCl_3 : HCl : H_2O = 1 : 26 : 192$.

10 c.c. solution used for each experiment: Time = 76 hours. Temperature = ordinary (summer).

	Molecules. $BiCl_3 : HCl : H_2O$	Percentage of $BiCl_3$ decomposed.
a.....	1 : 26 : 3,500	70·84
b.....	1 : 26 : 4,000	81·94
c.....	1 : 26 : 4,500	86·58
d.....	1 : 26 : 5,000	91·46
e.....	1 : 26 : 5,500	94·17
f.....	1 : 26 : 6,000	94·82
g.....	1 : 26 : 6,500	98·19
h.....	1 : 26 : 7,000	97·93
j.....	1 : 26 : 7,500	98·22
k.....	1 : 26 : 8,000	98·38
l.....	1 : 26 : 9,000	98·69
m.....	1 : 26 : 10,000	99·02
n.....	1 : 26 : 12,500	trace only undecomposed.
o.....	1 : 26 : 15,000	100·00

TABLE II.—*Influence of mass.*

52·727 grams Bi_2O_3 dissolved in 170·3 c.c. same aqueous HCl.

After solution have	71·317 grams	$BiCl_3$.	Solution No. 2.
	21·325 „	HCl.	
	151·162 „	H_2O.	

or in molecular proportions, $BiCl_3 : HCl : H_2O = 2 : 5 : 75 = 1 : 2·5 : 37·5$.

Series A.—10 c.c. solution used for each experiment. Time = 48 hours. Temperature = ordinary.

	Molecules. $BiCl_3 : HCl : H_2O$	Percentage of $BiCl_3$ decomposed.
a..	1 : 2·5 : 100	23·16
b..	1 : 2·5 : 500	93·22
c..	1 : 2·5 : 1,000	99·08
d..	1 : 2·5 : 1,260	99·65

Series B.—5 c.c. solution used for each experiment; other details as before.

e..	1 : 2·5 : 100	28·49
f..	1 : 2·5 : 500	93·11
g..	1 : 2·5 : 1,000	99·34
h..	1 : 2·5 : 1,250	99·67

TABLE III.—*Influence of mass.*

13·4682 grams Bi_2O_3 dissolved in 46 c.c. prepared acid.

After solution have	18·2166	grams $BiCl_3$.	Solution No. 3.
	6·1222	„ HCl.	
	40·7414	„ H_2O.	

or in molecular proportions, $BiCl_3 : HCl : H_2O = 1 : 3 : 40$.

10 c.c. solution used for each experiment. Time = 76 hours. Temperature = ordinary.

Molecules. $BiCl_3 : HCl : H_2O$	Percentage of $BiCl_3$ decomposed.
1 : 3 : 245	56·12
1 : 3 : 490	95·45
1 : 3 : 735	97·47
1 : 3 : 1,000	99·12

TABLE IV.—*Influence of mass.*

3·757 grams BiOCl dissolved in 13 c.c. prepared acid.

After solution have	4·547	grams $BiCl_3$.	Solution No. 4.
	2·4625	„ HCl.	
	11·3337	„ H_2O.	

or in molecular proportions, $BiCl_3 : HCl : H_2O = 1 : 4 : 40$.

Molecules. $BiCl_3 : HCl : H_2O$	Percentage of $BiCl_3$ decomposed.
1 : 4 : 500	67·93
1 : 4 : 1,000	98·53
1 : 4 : 1,500	99·62

4. The number of water molecules present exerts a most marked influence upon the course of the chemical change. It is very probable that the addition of a small quantity of water to a solution containing bismuthous chloride and hydrochloric acid, causes the decomposition of a few of the former molecules, but if this be so, it is evident that the reverse action ($BiOCl + 2HCl = BiCl_3 + H_2O$) takes place, the result being an apparent maintenance of the original state of equilibrium. In order that the primary action shall preponderate over the reverse action, the number of water molecules must be very large as compared with that of hydrochloric acid molecules present.

5. If the initial and final states of the reacting system be alone taken into consideration, a definite proportion is found to hold between the number of hydrochloric acid and of water molecules.

Certain of the intermediate states of the system will be considered in the sequel.

To find the proportion existing between the numbers of the various molecules present, when the whole of the bismuthous chloride is converted into oxychloride, it is of course requisite that the hydrochloric acid produced in the reaction ($BiCl_3$ produces 2HCl) be taken into account. This being done, the general result is that from 450 to 460 molecules of water must be present for each molecule of hydrochloric acid, in order that one molecule of bismuthous chloride may be completely converted into bismuthyl chloride. In No. 1 solution the molecular proportion at the close of the action was $BiCl_3 : HCl : H_2O = 1 : 1 : 450$; in No. 2 = 1 : 1 : 460; and in No. 4 = 1 : 1 : 450. As the reaction was not carried to entire completion in No. 3 solution, the numbers obtained with that liquid are omitted in this calculation.

When it is remembered that the three liquids contained very different absolute quantities of the reacting bodies, and also when the results detailed in Table II, Series A, are compared with those in the same table, Series B, I think it is evident that the general result just stated holds good, independently of the original degree of concentration of the liquids, and of the absolute amount of liquid used.

Some of the results detailed in Tables I to IV are graphically represented by the curves of Table A.

6. Let me consider the influence of time upon the reaction under consideration. The numerical results obtained are arranged in Tables V, VI, and VII, and graphically in the curves of Table B. The broken curves of Table C represent some of the numerical results of Table VII.

It is apparent from these numbers that when comparatively few water molecules are present chemical change proceeds with no great velocity, and that when, in round numbers, three-fourths of the total decomposition is accomplished, the velocity of the change greatly diminishes. If, however, large numbers of water molecules be present, the total change is accomplished in an exceedingly short space of time, the amount of change being indeed independent of the time of action. If the amount of water added be sufficient to decompose the greater part but not the whole of the bismuthous chloride present, then it is found that a state of what appears to be stable equilibrium is very quickly established in the reacting system, and that this state is maintained for periods of time amounting certainly to 14 days. My experiments do not allow me to say positively whether this equilibrium is finally disturbed or not, but I am inclined to believe that the action of time alone is insufficient to produce any larger amount of chemical change. When 8,000 water molecules are present for each molecule of bismuthous chloride and of hydrochloric acid, a state of practically

stable equilibrium is attained in ten minutes, by the system of bismuthous chloride, bismuthyl chloride, hydrochloric acid, and water molecules, and this state is scarcely changed after the expiry of 14 days. Experiments with solutions of calcium chloride and sodium carbonate, to be detailed in the sequel, show that the state of equilibrium attained in this case, after two or three hours, is maintained unchanged after the expiry of 39 days.

TABLE V.—*Influence of time.* (Compare curves of Table B).

Solution No. 1. $BiCl_3 : HCl : H_2O = 1 : 26 : 192$ mols.

Molecules. $BiCl_3 : HCl : H_2O$	Time.	Percentage of $BiCl_3$ decomposed.
1 : 26 : 3,500	53 mins.	30·03
	48 hours	67·85
	76 „	70·84
	9 days	70·70*
1 : 26 : 5,500	76 hours	94·17
	14 days	94·95
1 : 26 : 6,000	76 hours	94·82
	14 days	95·71
1 : 26 : 6,500	76 hours	98·19
	14 days	96·47
1 : 26 : 7,500	30 mins.	97·09
	8 hours	97·55
	18 „	98·08
	76 „	98·22
1 : 26 : 8,000	10 mins.	95·39
	76 hours	98·38
	14 days	97·78
1 : 26 : 9,000	76 hours	98·69
	14 days	99·31
1 : 26 : 10,000	10 mins.	98·48
	76 hours	99·02
	14 days	99·40
1 : 26 : 12,500	76 hours	trace only undecomposed.
	14 days	„ „

* In this experiment the $BiCl_3$ solution was added, in small successive portions, to the water.

TABLE VI.—*Influence of time.*

Solution No. 2. $BiCl_3 : HCl : H_2O = 1 : 2{\cdot}5 : 37{\cdot}5$ mols.

Molecules. $BiCl_3 : HCl : H_2O$	Time.	Percentage of $BiCl_3$ decomposed.
1 : 2·5 : 500	48 hours	93·22
	14 days	93·99
1 : 2·5 : 1,000	48 hours	99·08
	14 days	99·36
1 : 2·5 : 1,250	48 hours	99·65
	14 days	99·68

TABLE VII.—*Influence of time.* (Compare broken curves of Table C.)

Solution No. 1. $BiCl_3 : HCl : H_2O = 1 : 26 : 192$ mols. "Surface addition" (see p. 322).

Molecules. $BiCl_3 : HCl : H_2O$	Time.	Percentage of $BiCl_3$ decomposed.
1 : 26 : 2,900	3 mins.	12·19
	35 „	23·26
	24 hours	46·99
	76 „	60·20
1 : 26 : 3,000	3 mins.	18·61
	35 „	27·09
	24 hours	50·91
	76 „	64·45
1 : 26 : 3,500	3 mins.	50·26
	35 „	50·52
	48 hours	68·85

7. The following equation presents a general statement of the action of water upon bismuthous chloride, in presence of hydrochloric acid:—

$$x\mathrm{BiCl_3} + x'\mathrm{HCl} + x''\mathrm{H_2O} = (x - n)\mathrm{BiOCl} + n\mathrm{BiCl_3} + \{x' + 2(x - n)\}\mathrm{HCl} + \{x'' - (x - n)\}\mathrm{H_2O}.$$

The greater the value of x'' on the left-hand side of the equation—the values of x and x' being constant—the more rapidly will a condition of equilibrium be attained among the reacting molecules; the smaller also will be the value of n; if x'' be very large, the element of time may be neglected. If x'' have a small value, the value of n will vary at different moments, and this value will always remain somewhat large.

8. I have already considered the case in which n becomes equal to zero, and have shown that the value of x'' varies from 450 to 460 times

TABLE B. *(For numerical details see Tables V and VI.)*

INFLUENCE OF TIME.

Nº 1 Solution. Temperature = ordinary. Initial state = $BiCl_3 : HCl : H_2O = 1 : 26 : 192$ mols.

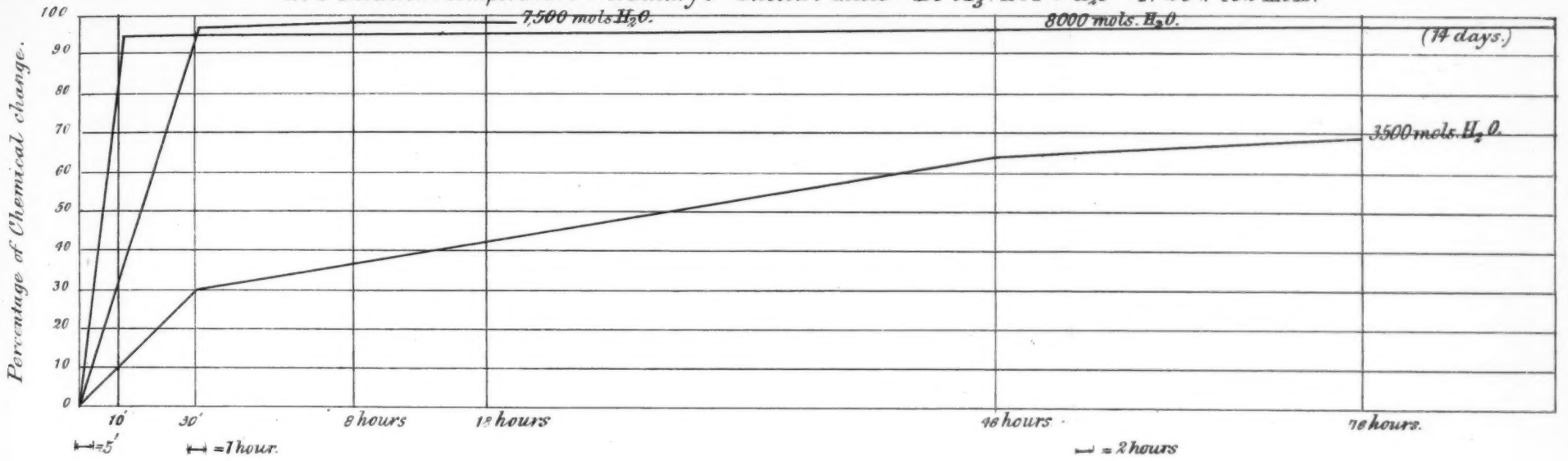
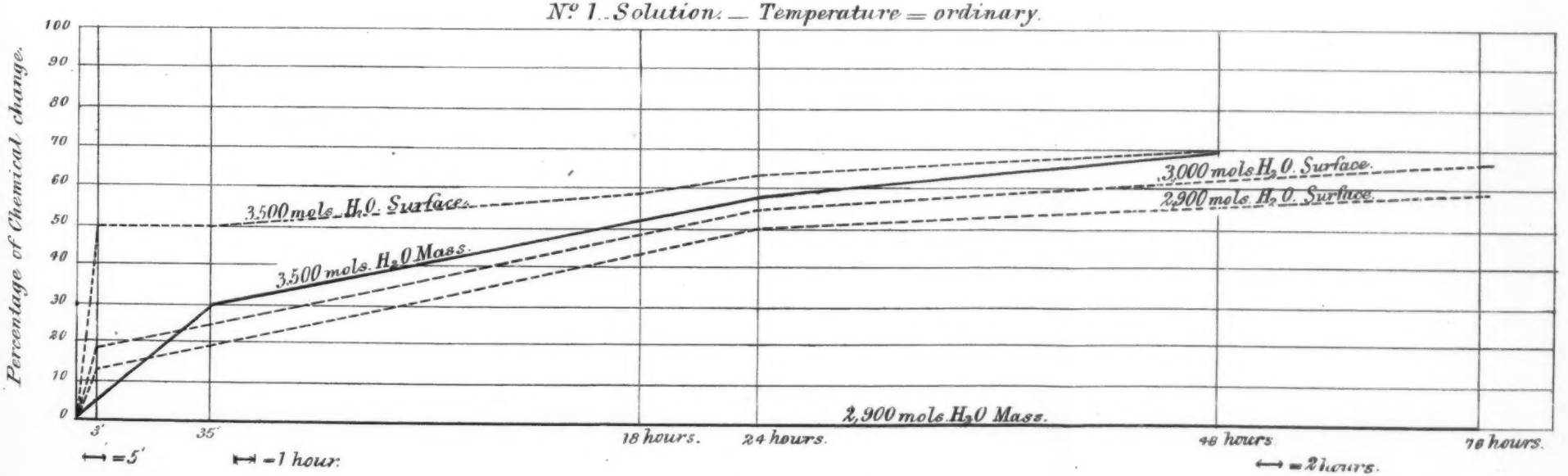


TABLE C. *(For numerical details see Tables VII and X.)*

INFLUENCE OF MANNER OF MIXING.

Nº 1. Solution. — Temperature = ordinary.



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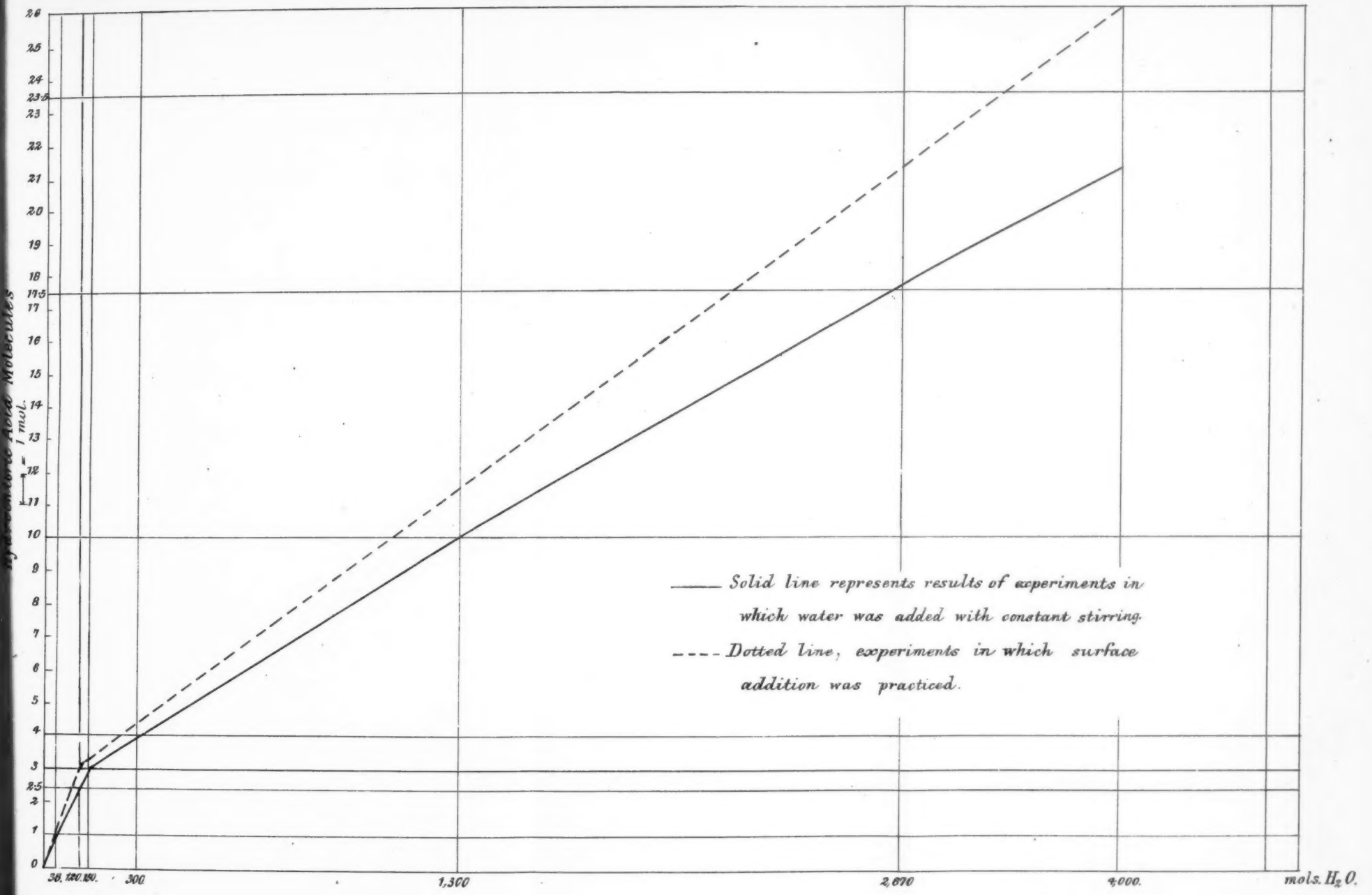
TABLE_D. (For numerical details see Tables VIII and IX.)

INFLUENCE OF RELATION BETWEEN ACID AND WATER MOLECULES UPON COURSE OF CHEMICAL CHANGE.

Bismuthous Chloride molecules=1.



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x'. I now wish to consider the case in which n is approximately equal to x, that is, I wish to consider the distribution of mass when the permanent formation of bismuthyl chloride just commences. The numerical results bearing upon this subject are arranged in Table VIII. The numbers obtained are merely approximate. Small differences in the method of adding water cause considerable differences in the results. This will be apparent by comparing the numbers of Series A with those of Series B. "Surface addition" will be explained in the sequel. These results show that in order to establish permanent production of bismuthyl chloride molecules, the value of x'' must be increased in a more rapidly increasing ratio (referred to the value of x) than that of x', that is to say, if x be equal to 1, and if x' be increased from 1 to 2, the value of x'' must be more than doubled.

The numbers showing the proportions required to exist between x' and x'' in different experiments are to be found in Table VIII. The curves of Table D graphically represent the principal results detailed in Table VIII, Series A and B.

TABLE VIII.—*Equilibrium of mixtures of $BiCl_3$, HCl, and H_2O molecules.* (Compare curves of Table D.)

Solutions of $BiCl_3$ in aqueous HCl; H_2O added until permanent precipitate of BiOCl just formed.

Series A.—"Mass addition" of H_2O.

	Precipitation permanent. Molecules.				Proportion of HCl to H_2O mols.
a..	$BiCl_3$	HCl	H_2O	= 1 : 1 : 38	1 : 38
b..	,,	,,	,,	= 1 : 2·5 : 120	1 : 55
c..	,,	,,	,,	= 1 : 3 : 150	1 : 56
d..	,,	,,	,,	= 1 : 4 : 300	1 : 87
e..	,,	,,	,,	= 1 : 10 : 1,300	1 : 131
f..	,,	,,	,,	= 1 : 17·5 : 2,670	1 : 152
g..	,,	,,	,,	= 1 : 23·5 : 4,120	1 : 175
h..	,,	,,	,,	= 1 : 35 : 7,230	1 : 208

Series B.—"Surface addition" of H_2O.

j..	$BiCl_3$	HCl	H_2O	= 1 : 1 : 38	1 : 38
k..	,,	,,	,,	= 1 : 2·5 : 103	1 : 42
l..	,,	,,	,,	= 1 : 3 : 120	1 : 40
m..	,,	,,	,,	= 1 : 4 : 275	1 : 69
n..	,,	,,	,,	= 1 : 26 : 3,090	1 : 119

The proportions found to exist between x' and x'' are further developed in Table IX.

TABLE IX.—*Equilibrium of $BiCl_3$, HCl, and H_2O molecules* (continued).

Proportions between HCl and H_2O mols.—for one mol. $BiCl_3$—in order that BiOCl may be permanently formed. (Compare results of preceding Table.)

Series A.—Table VIII.

HCl mols. (x') in	×	= HCl mols. in	H_2O mols. (x'') in	×	= H_2O mols. in	Proportion between numbers by which HCl and H_2O mols. must be multiplied =
Exp. *a*	2·5	Exp. *b*	Exp. *a*	3	Exp. *b*..	1 : 1·2
„ *a*	3	„ *c*	„ *a*	4	„ *c*..	1 : 1·3
(„ *b*	1·2	„ *c*	„ *b*	1·25	„ *c*)	
„ *a*	4	„ *d*	„ *a*	8	„ *d*..	1 : 2
(„ *c*	1·3	„ *d*	„ *c*	2	„ *d*)	
„ *a*	10	„ *e*	„ *a*	34	„ *e*..	1 : 3·4
(„ *d*	2·5	„ *e*	„ *d*	4·3	„ *e*)	
„ *a*	17·5	„ *f*	„ *a*	70	„ *f*..	1 : 4
(„ *e*	1·75	„ *f*	„ *e*	2·05	„ *f*)	
„ *a*	23·5	„ *g*	„ *a*	109	„ *g*..	1 : 4·6
(„ *f*	1·35	„ *g*	„ *f*	2·7	„ *g*)	
„ *a*	35	„ *h*	„ *a*	190	„ *h*..	1 : 5·4
(„ *g*	1·5	„ *h*	„ *g*	1·75	„ *h*)	

Series B.—Table VIII.

Exp. *j*	2·5	Exp. *k*	Exp. *j*	2·7	Exp. *k*..	1 : 1·08
„ *j*	3	„ *l*	„ *j*	3·2	„ *l*..	1 : 1·07
(„ *k*	1·2	„ *l*	„ *k*	1·17	„ *l*)	
„ *j*	4	„ *m*	„ *j*	7·3	„ *m*.	1 : 1·82
(„ *l*	1·3	„ *m*	„ *l*	2·3	„ *m*)	
„ *j*	26	„ *n*	„ *j*	81	„ *n*..	1 : 3·1
(„ *m*	6·5	„ *n*	„ *m*	11·5	„ *n*)	

9. It appears, therefore, that if there be a sufficient number of water molecules present to neutralise the action of the acid molecules to such an extent as shall admit of the permanent formation of bismuthyl chloride molecules, and if the number of acid molecules be then doubled, that an equal amount of neutralising action is ensured only when the number of water molecules is more than doubled. When the initial equilibrium of the system is permanently disturbed, but without the production of a new permanently stable equilibrium, the production of this disturbance is dependent, not only upon the relative, but also upon the absolute number of molecules present. On the other hand the production of an entirely new and permanent state of equilibrium

is dependent only upon the relative numbers of molecules present. The study of the course of the chemical change under consideration exhibits molecular phenomena somewhat different from those which are apparent if the initial and final states of molecular distribution be alone examined. It will be shown hereafter that the results obtained from an examination of the action formulated, $MCl_2 + M'_2CO_3 = 2M'Cl + MCO_3$ (page 326), points to a conclusion similar to that just stated.

10. It is evident that our ordinary system of chemical notation expresses only the initial and final distributions of mass of a system, which more or less rapidly passes from one configuration to another; but the final result thus obtained always represents the stable equilibrium of a system acted on by many forces: if an advantage be given to one of these during the process of change, the final distribution of mass may be largely altered. Special instances of the action of such external aids are considered in Part II of the present paper.

11. I have already pointed out (par. 6, p. 316) that, if water be added in quantity sufficient to decompose the greater portion, but not the whole of the bismuthous chloride present, a state of what appears to be permanently stable equilibrium is quickly established in the reacting system.

So far as my experiments extend, they justify the statement that the production of this state is dependent only upon the relative numbers of water and acid molecules. Thus in solution No. 2 the initial molecular distribution in which is, $BiCl_3 : HCl : H_2O = 1 : 2{\cdot}5 : 37{\cdot}5$, the addition of such an amount of water as serves to alter these proportions to $1 : 2{\cdot}5 : 537{\cdot}5$ is accompanied with the decomposition of about 95 per cent. of the bismuthous chloride originally present, and this state of equilibrium remains unchanged for a very considerable time. If the molecular proportion in solution No. 3 be $1 : 3 : 650$, a practically stable state of equilibrium (95 per cent. of decomposition) is attained; similarly an analogous condition is ensured in No. 4 solution when the molecular proportion is $1 : 4 : 1{,}000$; and in No. 1 solution the necessary proportion is $1 : 26 : 6{,}000$. Now in each of these solutions, the presence of from 200 to 230 molecules of water for each molecule of hydrochloric acid, *independently of the absolute number* of the latter molecules, causes an equal amount of decomposition, which amount marks the assumption of a practically stable condition of equilibrium of the reacting system.

12. It would thus appear that if we allow any system of bismuthous chloride, hydrochloric acid, and water molecules, in which the number of the last-named molecules is large, to act and react until a new and permanent configuration be gained, this configuration will be dependent upon the relation between the numbers of acid and water molecules;

but that if the mutual molecular actions be stopped before such a permanent configuration is gained, the intermediate configuration will be largely dependent upon the absolute number of acid and water molecules present. In the first rush and bustle of the reacting molecules, the water molecules appear to get entangled among the acid molecules, and so to be impeded in their action on the molecules of bismuthous chloride; the greater the number of acid molecules the greater is the amount of this entanglement, although there may be proportionately as many water molecules present as when the number of acid molecules was small. But give the system time, and the water molecules will free themselves from their entanglements; so that the same final state of the system will be attained, whether there be originally many or few molecules of water.

13. In those experiments, the results of which have now been detailed, water was added from a measuring vessel to an acid solution of bismuthous chloride, which was maintained in constant agitation. If the water be poured very cautiously on to the surface of the bismuth solution, and if the whole be then suddenly shaken up, a new set of phenomena present themselves. This method of addition of water I have called "surface addition;" and in Table X I have contrasted the results obtained by this method with those obtained by "mass addition," other conditions being the same in each series of experiments. Some of these results are represented graphically in the curves of Table C.

TABLE X.—*Comparison of results obtained by "surface addition" with those obtained by "mass addition" of water.* (Compare curves of Table C.)

Molecules. $BiCl_3 : HCl : H_2O$	Time.	Percentage of $BiCl_3$ decomposed. "Surface addition."	"Mass addition."
1 : 26 : 2,900	3 mins.	12·19	0·00
	35 „	23·26	
	24 hours	46·99	
	76 „	60·20	
1 : 26 : 3,000	3 mins.	18·61	0·00
	35 „	27·09	
	24 hours	50·91	
	76 „	64·45	
1 : 26 : 3,500	3 mins.	50·26	0·00
	35 „	50·52	30·03
	48 hours	68·85	67·85
	76 „	—	70·84
	9 days	—	70·70
1 : 2·5 : 66	48 hours	0·07	0·00
1 : 2·5 : 70	„	9·00	

In the "surface addition" series formation of bismuthyl chloride was apparent at the surfaces of contact of the layers of water and of bismuthous chloride dissolved in hydrochloric acid.

14. These results show that if a few molecules of bismuthyl chloride be allowed to form, it is comparatively very hard to unform these molecules; but that it is possible to arrange the conditions of the experiment so that none of these molecules are permanently produced, although a greater number of water molecules be present than in the first experiment.

At the surfaces of the layers of contact of the two liquids in the "surface addition" experiments, we have such an arrangement as admits of the formation of bismuthyl chloride molecules in the presence of comparatively few hydrochloric acid molecules; it is not until the former molecules have passed downwards towards the lower part of the vessel that there is any chance of their meeting large numbers of acid molecules. If, however, "mass addition" be practised, each bismuthyl chloride molecule so soon as formed finds itself surrounded by a large number of acid molecules, so that its existence is but ephemeral.

15. It is somewhat remarkable that two systems may be obtained consisting of approximately the same absolute and the same relative numbers of water, acid, and bismuthous chloride molecules, that one of these may be perfectly stable, but that the other may undergo a continuous change of molecular equilibrium. Thus the "mass addition" of 2,900 mols. of water to No. 1 solution caused no precipitation of bismuthyl chloride even after 76 hours; while, when the same number of water molecules was added by "surface addition" to an equal volume of the same solution, 12 per cent. of the bismuthous chloride was decomposed in three minutes, and about 70 per cent. in 76 hours. If, however, such an amount of water be added by "mass addition" as causes the permanent precipitation of a small quantity of bismuthyl chloride, and if this solution be compared with a similar solution to which an equal amount of water has been added by "surface addition," the final states of equilibrium are found to be the same in both. Examples of this will be found in the numbers of Table X, some of which are also represented in the curves of Table C. (In one experiment, the bismuthous chloride solution was added to the water in small successive portions, the experiment extending over nine days; the *final* state of equilibrium was, however, the same as that attained in 48 hours under the ordinary conditions.)

16. The amount of bismuthous chloride decomposed in "surface addition" experiments, in short times, is always greater than that decomposed in analogous "mass addition" experiments in long times: the two amounts are equal. We must surely then believe that when

water is added to a solution of bismuthous chloride in hydrochloric acid with constant stirring, molecules of bismuthyl chloride are formed, but are instantly again decomposed; that there are atomic interchanges going on, but that these changes are balanced by those, and that therefore the entropy* of the system is constant. Give one set of changes a small advantage over the other; in other words, disturb the entropy of the system, and a new configuration is produced, and this again is succeeded by another, until a permanently stable state is attained.

If the experiment be so arranged that the entropy of the system is altered in the early stages of the experiment, the chemical change thus produced has evidently a start, so to speak, over another analogous change, which is produced by a change of entropy accomplished towards the later stages of the experiment; but the two changes having been made, the course of decomposition will proceed in each until one and the same final state of equilibrium is attained.

Is there not in these experiments a phenomenon somewhat analogous with that presented by supersaturated solutions?

17. The experiments detailed in Table X also confirm the remark made on page 321, that the study of the course of a chemical change often presents phenomena different from those attendant upon the initial and final stages of that change.

18. In a paper communicated to the Society about a year ago (Journal, 1878, *Trans.* 27) I gave some measurements illustrative of the course of the change formulated generally as $[x\mathrm{CaCl_2} + x'\mathrm{M_2CO_3} = (x - n)\mathrm{CaCO_3} + n\mathrm{CaCl_2} + 2x' - n'\mathrm{MCl} + n'\mathrm{M_2CO_3}]$; where M = Na or K. Since the date of that paper I have added considerably to the number of measurements made; these measurements I will now discuss.

The method of conducting the experiments was explained in the paper referred to.

Table XI contains the results of experiments bearing upon the influence of mass on the reaction under consideration. Many of these results are represented graphically in the curves of Table E.

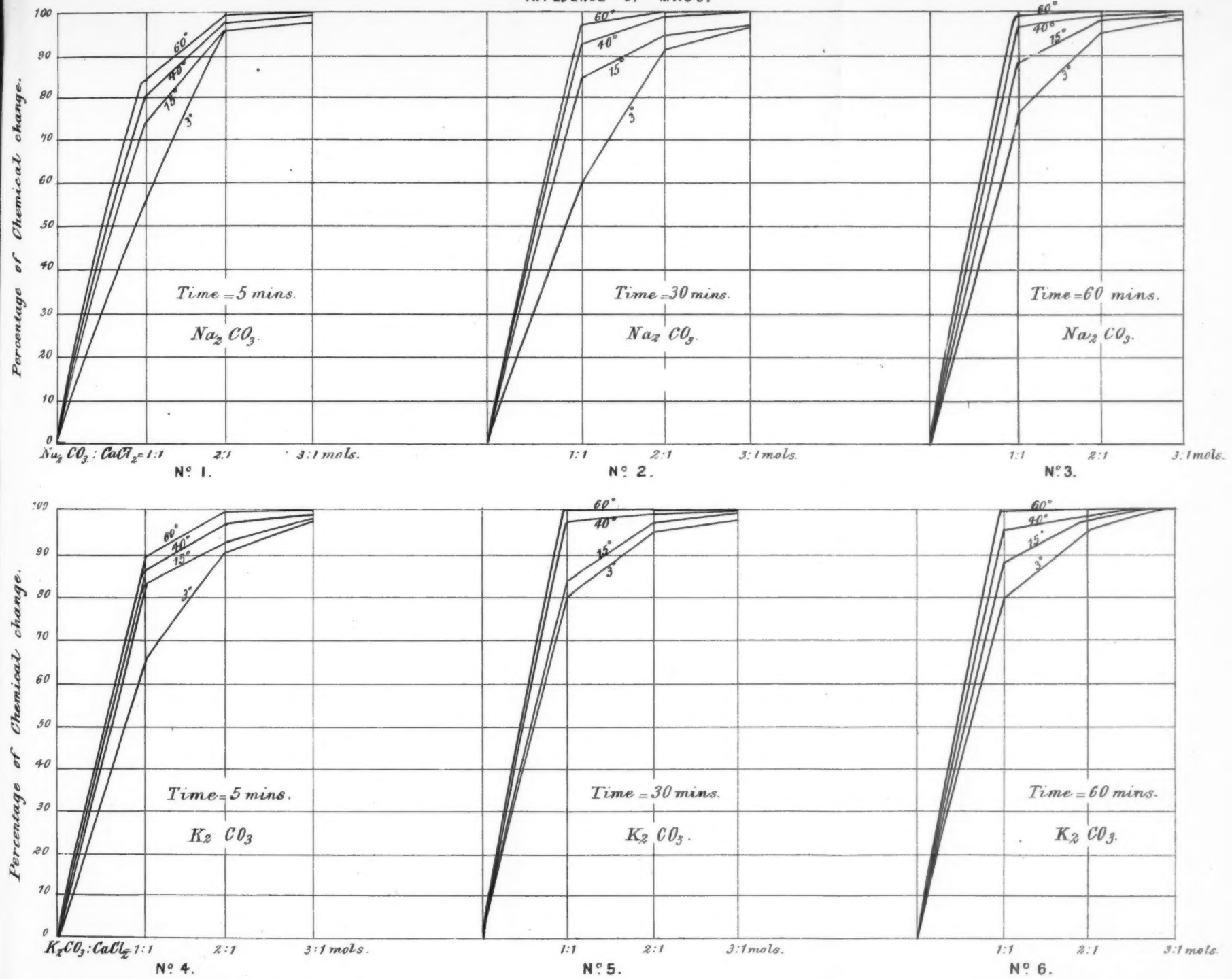
TABLE XI.—*Influence of mass.* (Compare curves of Table E.)

Total volume of liquid = 70 c.c. Various solutions of $\mathrm{CaCl_2}$ and $\mathrm{Na_2CO_3}$ (or $\mathrm{K_2CO_3}$) used; average amount of $\mathrm{CaCl_2}$ in mgms. = 100; average amount of $\mathrm{Na_2CO_3}$ in mgms. = 95·5.

* I use this term as meaning "internal energy of position" (see Clerk Maxwell's "Theory of Heat," p. 186), and not in the sense originally given it by Clausius, viz., as expressing energy inconvertible into mechanical work.

TABLE E. (For numerical details see Table XI.)

INFLUENCE OF MASS.



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Series A.—Time = 5 mins.

Molecules. $M_2CO_3 : CaCl_2$	Temperature.	Percentage of $CaCO_3$ produced, calculated on total theoretical yield. M = Na	M = K.
1 : 1	3°	53·5	64·0
2 : 1	,,	95·9	92·7
3 : 1	,,	96·7	96·0
1 : 1	15°	74·5	81·1
2 : 1	,,	92·1	92·5
3 : 1	,,	94·3	96·5
1 : 1	40°	83·0	85·5
2 : 1	,,	93·2	95·4
3 : 1	,,	96·5	96·5
1 : 1	60°	85·0	86·0
2 : 1	,,	96·0	99·0
3 : 1	,,	100·0	100·0

Series B.—Time = 30 mins.

1 : 1	3°	58·6	80·0
2 : 1	,,	92·8	96·0
3 : 1	,,	96·8	96·0
1 : 1	15°	85·0	84·7
2 : 1	,,	93·2	98·7
3 : 1	,,	96·4	98·7
1 : 1	40°	96·0	96·0
2 : 1	,,	99·0	99·0
3 : 1	,,	100·0	100·0
1 : 1	60°	92·8	100·0
2 : 1	,,	100·0	100·0
3 : 1	,,	100·0	100·0

Series C.—Time = 60 mins.

1 : 1	3°	76·3	80·0
2 : 1	,,	96·0	100·0
3 : 1	,,	96·0	100·0
1 : 1	15°	86·0	86·0
2 : 1	,,	95·3	100·0
3 : 1	,,	96·9	100·0
1 : 1	40°	96·0	96·0
2 : 1	,,	96·0	100·0
3 : 1	,,	100·0	100·0
1 : 1	60°	99·0	100·0
2 : 1	,,	100·0	100·0
3 : 1	,,	100·0	100·0

19. These experiments fully confirm the statement previously made, that at ordinary temperatures the change formulated $CaCl_2 + M_2CO_3 = 2MCl + CaCO_3$(M = Na or K) is not completed unless the mass of M_2CO_3 molecules be considerably in excess of that shown in the equation. When equal molecules of calcium chloride and sodium (or potassium) carbonate were employed, about 10 per cent. of the chloride remained undecomposed even after 39 days' action.

A practically stable state of equilibrium is quickly attained by the reacting system of calcium chloride, calcium carbonate, sodium chloride, and sodium carbonate molecules: a similar phenomenon has been noticed in the reaction of water upon bismuthous chloride dissolved in hydrochloric acid (see par. 6, p. 316).

20. In both cases it appears that when the number of calcium chloride (or bismuthous chloride) molecules becomes very small compared with the numbers of the other molecules present, the former molecules seldom come within the sphere of action of the latter, or more probably, in the case of bismuthous chloride at any rate, that when they do come within the sphere of action and are thereby decomposed, they are immediately reformed. In other words, we find that before the whole of the internal energy of position of the reacting system has been expended the system has attained a condition of equilibrium. In the case of calcium chloride, as will be shown in the sequel, very small disturbances are sufficient to upset this equilibrium, and to cause the change to proceed to completion (compare par. 23).

21. The influence of time upon the chemical change under consideration is marked: it is illustrated by the numbers of Table XII, many of which are graphically represented in the curves of Table F.

TABLE XII.—*Influence of Time.* (Compare curves of Table F.)

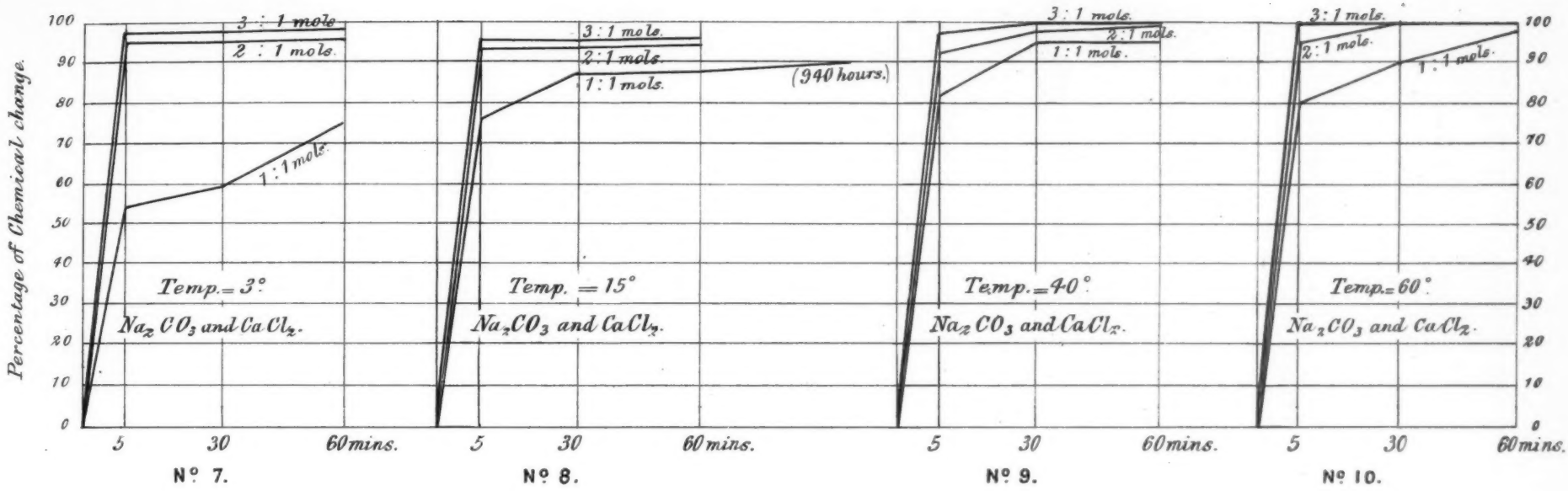
Total volume of liquid = 70 c.c. Other details as before.

Time.		Temperature.	Percentage of $CaCO_3$ produced. M = Na.	M = K.
5 min.	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	3°	53·5	64·0
30 „	„ „	„	58·6	80·0
60 „	„ „	„	76·3	80·0
39 days	„ „	„	89·6*	—
5 „	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	95·9	92·7
30 „	„ „	„	92·8	96·0
60 „	„ „	„	96·0	100·0

* This experiment proceeded during the Christmas vacation. The temperature probably did not rise above 5° at any time during the experiment.

TABLE F. (For numerical details see Table XII.)

INFLUENCE OF TIME.



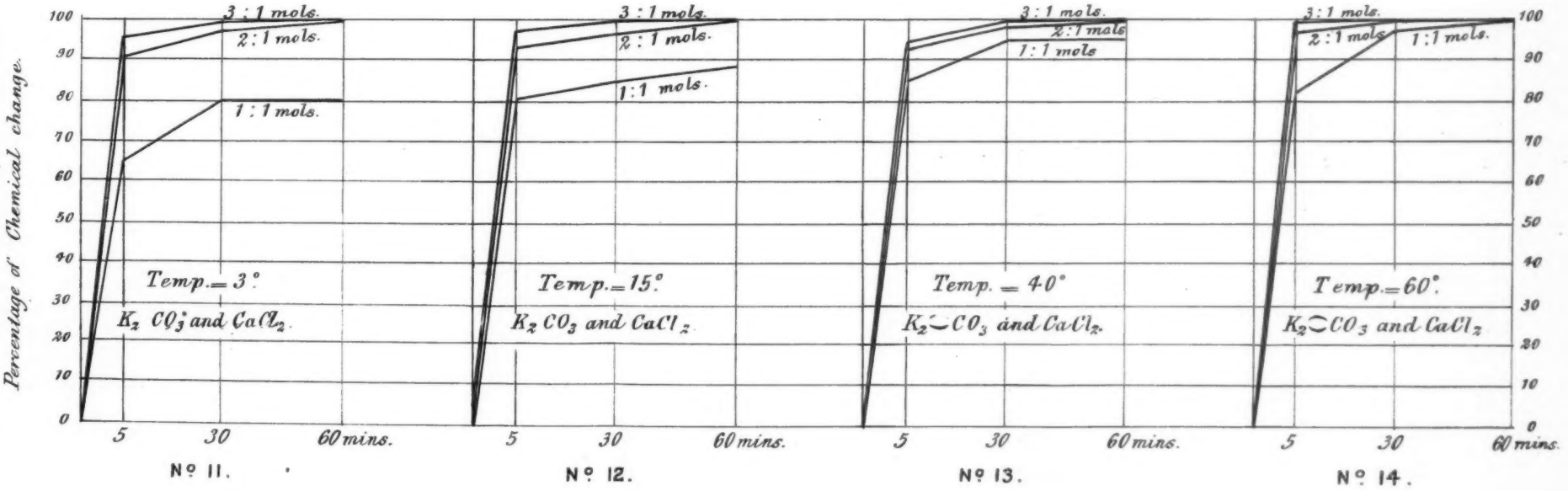


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TABLE XII (*continued*).

Time.		Temperature.	Percentage of $CaCO_3$ produced. M = Na.	M = K.
5 min.	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	8°	96·7	96·0
30 „	„ „	„	96·8	96·0
60 „	„ „	„	96·0	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	15°	74·5	81·1
30 „	„ „	„	85·0	84·7
60 „	„ „	„	86·0	86·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	92·1	92·5
30 „	„ „	„	93·2	98·7
60 „	„ „	„	95·3	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	„	94·3	96·5
30 „	„ „	„	96·4	98·7
60 „	„ „	„	96·9	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	40°	83·0	85·5
30 „	„ „	„	96·0	96·0
60 „	„ „	„	96·0	96·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	93·2	95·4
30 „	„ „	„	99·0	99·0
60 „	„ „	„	96·0	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	„	96·5	100·0
30 „	„ „	„	100·0	100·0
60 „	„ „	„	100·0	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	60°	85·0	86·0
30 „	„ „	„	92·8	100·0
60 „	„ „	„	99·0	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	96·0	99·0
30 „	„ „	„	100·0	100·0
60 „	„ „	„	100·0	100·0
5 „	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	„	100·0	100·0
30 „	„ „	„	100·0	100·0
60 „	„ „	„	100·0	100·0

The influence of time is evidently conditioned by the masses of the reacting bodies, and by the temperatures at which the action proceeds. With a constant temperature and equal numbers of molecules of chloride and carbonate, an increase in the time of action is always accompanied by an increase in the amount of change. The latter increase is most marked after the expiry of the first portion of the time. The only exception to the latter part of this rule (see Experiments 2 and 3, Table XII, and curve 7, Table F) is to be explained either as an experimental error, or possibly as pointing to the forma-

tion of some hydrate of sodium carbonate or calcium chloride at the low temperature of the experiment.

22. When the action approaches that point at which equilibrium is established, the influence of time becomes feebly marked; the molecules of chloride and carbonate, being now few in number, seldom come into collision. Inasmuch as, with an increased mass of carbonate molecules, this state of more or less permanent equilibrium is quickly attained, the influence of time is less marked when 2 or 3 molecules of carbonate are added, than when but a single molecule (proportionately to the chloride molecules) is employed.

23. If the influence of time upon the chemical change considered in the first part of this paper be compared with the influence of the same variable upon the change now under consideration, a difference is at once noticed. In the first case it is necessary to add a very large number of water molecules in order to complete the change, the amount of change is then practically independent of the time: in the second case, a very much smaller number of alkaline carbonate molecules—proportionately to the calcium chloride molecules—is required to complete the change; the amount of change also varies considerably at different moments of time.

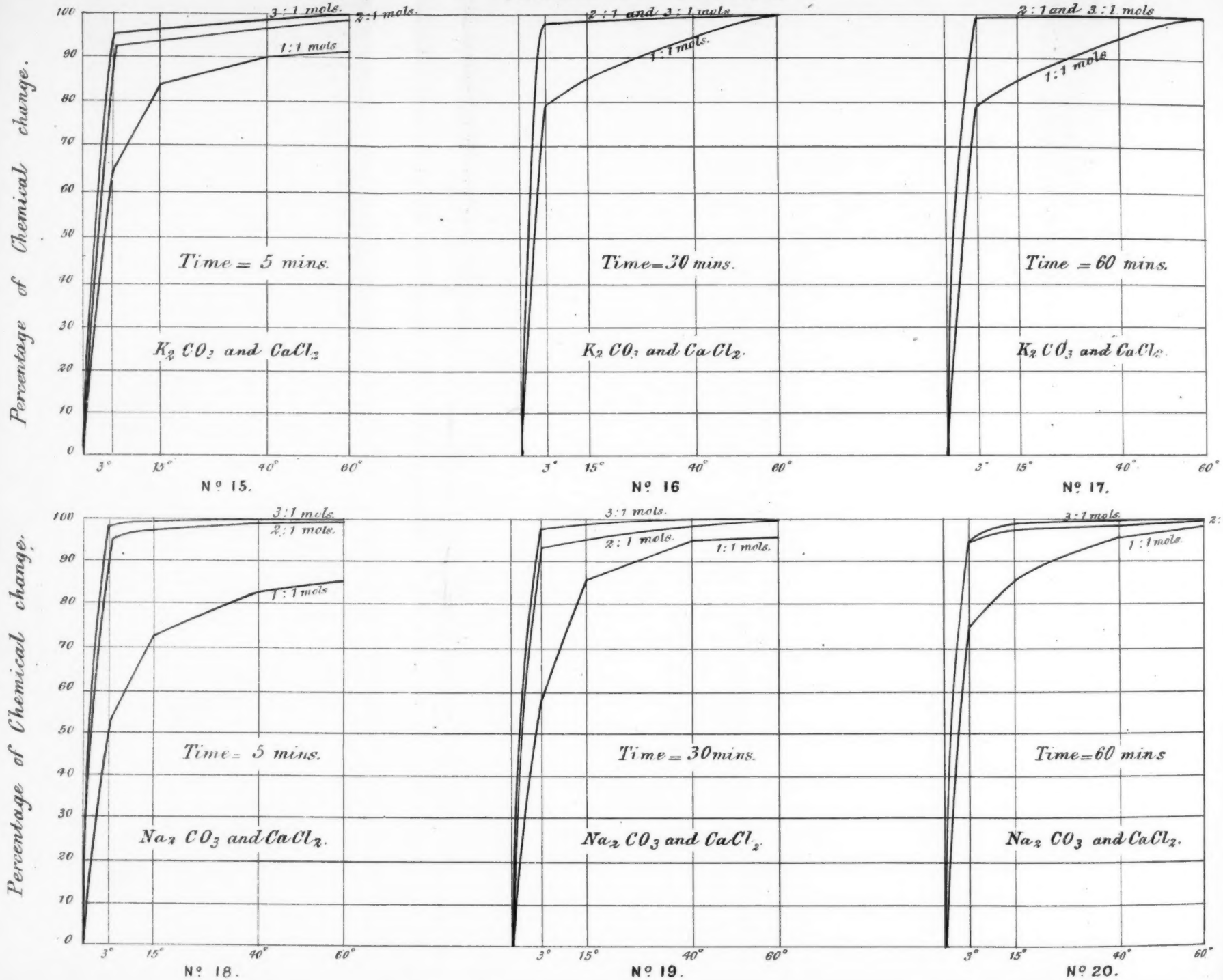
In the former case it appears that the production of a small amount of change is accompanied with but small variations in the entropy of the reacting system, the change therefore proceeds slowly and comes to a standstill, while there are yet comparatively large numbers of undecomposed bismuthous chloride molecules present—unless indeed very large masses of water are added, in which case there is a sudden disturbance in the entropy of the system. In the case of the decomposition of calcium chloride it appears that a small amount of chemical change involves a considerable variation in the entropy of the system: hence, give time, and even with *comparatively* small masses, the change will complete itself.

I have been unable to find any exact measurements of the thermal reactions connected with the formation of $CaCl_2$ and $CaCO_3$, and with $BiCl_3$ and BiOCl respectively; but I think that the facts known concerning the decomposition of $CaCl_2$ tend to show that in the formation of $CaCO_3$ there is probably considerably more heat evolved than in the formation of $CaCl_2$: while facts which I have myself communicated to the Society concerning the oxidation of $BiCl_3$ (Journal, **2**, 1877, 136, and *Trans.*, 1878, 192) show that this body is not readily decomposed into BiOCl, and that therefore the heat evolution involved in such an oxidation is probably not large.

24. I will now consider the influence of temperature upon the decomposition of calcium chloride by alkaline carbonate. The results

TABLE G. (*For numerical details see Table XIII.*)

INFLUENCE OF TEMPERATURE.



are arranged in Table XIII, and graphically in the curves of Table G.

TABLE XIII.—*Influence of Temperature.* (Compare curves of Table G.)

Total volume of liquid = 70 c.c. Other details as before.

Temperature.		Time.	Percentage of $CaCO_3$ produced. M = Na.	M = K.
3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	5 mins.	53·5	64·0
15	,, ,,	,,	74·5	81·1
40	,, ,,	,,	83·0	85·5
60	,, ,,	,,	85·0	86·0
3°	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	,,	95·9	92·7
15	,, ,,	,,	92·1	92·5
40	,, ,,	,,	93·2	95·4
60	,, ,,	,,	96·0	99·0
3°	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	,,	96·7	96·0
15	,, ,,	,,	94·3	96·5
40	,, ,,	,,	96·5	96·5
60	,, ,,	,,	100·0	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	30 mins.	58·6	80·0
15	,, ,,	,,	85·0	84·7
40	,, ,,	,,	96·0	96·0
60	,, ,,	,,	92·8	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	,,	92·8	96·0
15	,, ,,	,,	93·2	98·7
40	,, ,,	,,	99·0	99·0
60	,, ,,	,,	100·0	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	,,	96·8	96·0
15	,, ,,	,,	96·4	98·7
40	,, ,,	,,	100·0	100·0
60	,, ,,	,,	100·0	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	60 mins.	76·3	80·0
15	,, ,,	,,	86·0	86·0
40	,, ,,	,,	96·0	96·0
60	,, ,,	,,	99·0	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	,,	96·0	100·0
15	,, ,,	,,	95·3	100·0
40	,, ,,	,,	96·0	100·0
60	,, ,,	,,	100·0	100·0
3°	$CaCl_2 : M_2CO_3 = 1 : 3$ mols.	,,	96·0	100·0
15	,, ,,	,,	96·9	100·0
40	,, ,,	,,	100·0	100·0
60	,, ,,	,,	100·0	100·0

In the experiments made at 3°, beakers containing the proper quantities of water and alkaline carbonate solution, were surrounded by ice until the temperatures of the liquids were nearly constant, calcium chloride solution, at the same temperature, was then added, and the liquids were surrounded by ice until the moment arrived for filtration.

25. In my previous paper I stated that increase of temperature causes an increase in the amount of calcium chloride decomposed in a given time, other conditions being constant. The experiments now detailed confirm this result, but require that it be stated in a somewhat modified form.

The influence of temperature is very marked when equal molecules of calcium chloride and alkaline carbonate are allowed to react upon one another: when, however, two or more molecules of carbonate are employed, the influence of temperature in increasing, or decreasing, the amount of chemical change, although yet perceptible, becomes much less marked. That this is so will be at once apparent from the curves of Table G.

26. It has been already shown that when no excess of either reacting substance is present, a condition of practically stable equilibrium is attained by the system after a comparatively short time; but it is now shown that if energy be added to the system from without, this point of equilibrium is passed and a new equilibrium is attained, when the whole, or almost the whole, of the calcium chloride molecules have been decomposed. In the case of potassium carbonate, decomposition is complete at a temperature of 60° with equal numbers of molecules of carbonate and calcium chloride, and after 60 minutes' action; in the case of sodium carbonate about 1 per cent. of the chloride remains undecomposed under the same conditions.

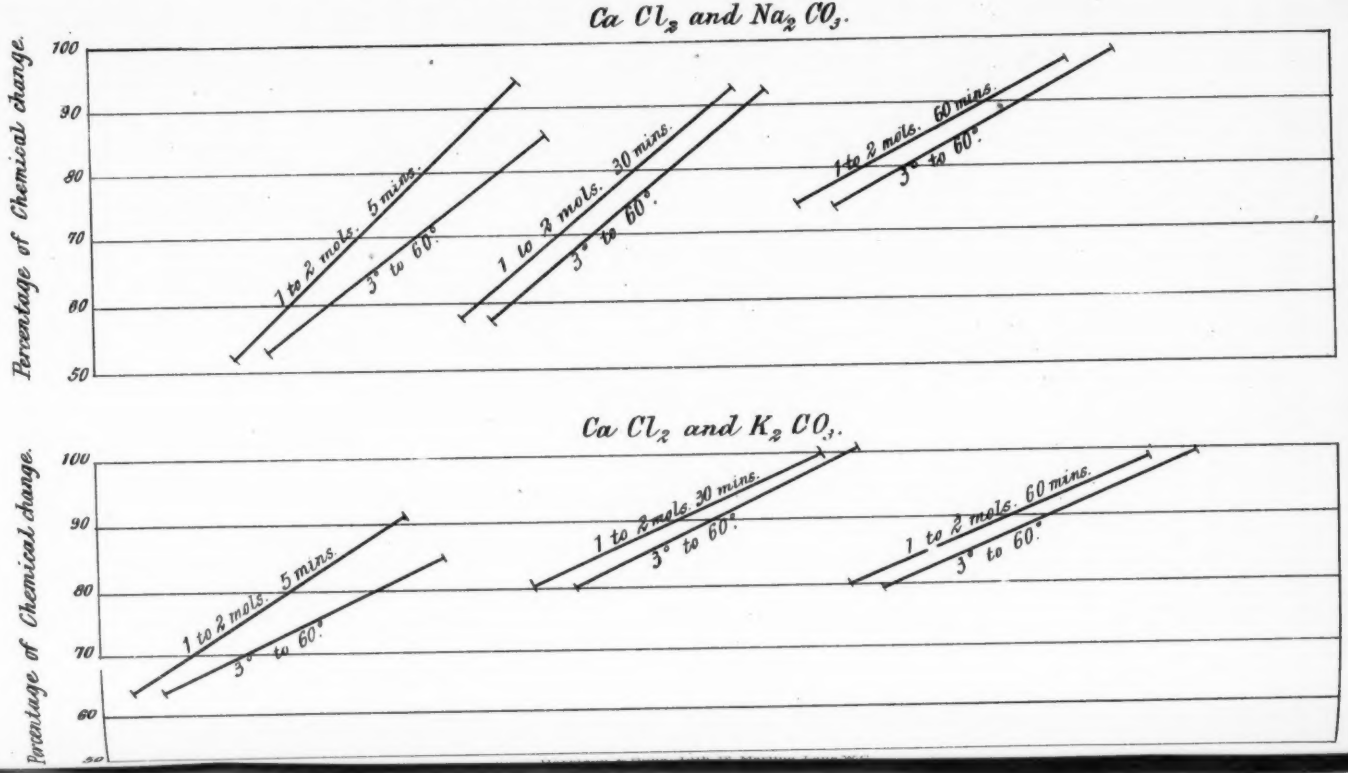
If, however, the mass of one of the reacting substances be considerably larger than that of the other, then the collisions and decompositions of the molecules are so numerous, even in a short time, that the addition of energy from without the system causes but little change in the final state. That such addition does cause some change in the final state is evident from the numbers detailed, but that this change is small compared with that produced when no excess of either of the reacting substances is employed is also apparent from these numbers.

27. If experiments were conducted in more dilute solutions than those which I have employed, it is probable that the influence of temperature would be more marked in cases where two or more molecules of alkaline carbonate are employed for one molecule of calcium chloride. I am at present conducting experiments to test the truth of this hypothesis.

28. It is worthy of remark that the influence of time is exerted differently from that of temperature in increasing the total amount of

TABLE H. (For numerical details see Table XIV.)

INFLUENCE OF TEMPERATURE COMPARED WITH THAT OF MASS.



change. Confining our attention to those decompositions in which equal molecules of the reacting bodies are employed, it is found that the influence of time is most marked at comparatively low temperatures. At such temperatures the molecular mobility of the system is comparatively small, hence it is necessary that time be given, in order that a new condition of equilibrium may be reached. At higher temperatures, the molecular mobility being greater, the new equilibrium is reached in a shorter time, but if there be no excess of either of the reacting compounds, a certain amount of time is required before this state can be attained; hence the influence of time is considerable even at high temperatures. But it appears that time alone does not suffice to complete the decomposition of the whole of the calcium chloride molecules unless a high temperature be also insured, and if this be insured a comparatively short time only is required. Thus at the ordinary temperature only 86 per cent. of the complete theoretical yield of calcium carbonate is obtained after 60 minutes' action, when equal molecules of potassium carbonate and calcium chloride are employed, and inasmuch as I have shown that in the case of sodium carbonate only 89 per cent. of the total calcium carbonate is formed after 39 days' action, I think I am justified in saying that if the reaction be allowed to proceed at low temperatures, 3—7°, equal numbers of molecules of potassium carbonate and calcium chloride would never succeed in completely decomposing one another; before the decomposition reached completion a condition of permanently stable equilibrium would be attained. But if the temperature be maintained at 60°, the reacting masses being the same as in the previous experiment, complete decomposition is brought about in 30 minutes.

29. If the effects of temperature be compared with those of mass (see Table XIV and curves of Table H), it is apparent that an increase of about 55° causes as great an increase in the amount of decomposition as is effected by doubling the relative number of alkaline carbonate molecules, provided the increased temperature be allowed to act through a somewhat long period of time. In short times, on the other hand, increasing the mass of one of the reacting bodies is more effectual, in accomplishing a greater amount of decomposition, than in raising the temperature.

TABLE XIV.—*Influence of Temperature compared with that of Mass.*
(Compare curves of Table H.)

	Time.	Temp.	Percentage of $CaCO_3$ produced. M = Na.	M = K.
a. $CaCl_2 : M_2CO_3 = 1 : 1$ mol.	5 mins.	3°	53·5	64·0
b. $CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	„	95·9	92·7

TABLE XIV (*continued*).

Difference in $CaCO_3$ produced between *a* and *b*.

M = Na.	M = K.
42·4	28·7

	Temp.		Time.	Percentage of $CaCO_3$ decomposed. M = Na.	M = K.
c.	3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	5 mins.	53·5	64·0
d.	60	„ „	„	85·0	86·0

Difference in $CaCO_3$ produced between *c* and *d*.

M = Na.	M = K.
31·5	22·0

		Time.	Temp.		
e.	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	30 mins.	3°	58·6	80·0
f.	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	„	92·8	96·0

Difference in $CaCO_3$ produced between *e* and *f*.

M = Na.	M = K.
34·2	16·0

	Temp.		Time.		
g.	3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	30 mins.	58·6	80·0
h.	60	„ „	„	92·8	100·0

Difference in $CaCO_3$ produced between *g* and *h*.

M = Na.	M = K.
34·2	20·0

		Time.	Temp.		
j.	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	60 mins.	3°	76·3	80·0
k.	$CaCl_2 : M_2CO_3 = 1 : 2$ mols.	„	„	96·0	100·0

Difference between $CaCO_3$ produced in *j* and *k*.

M = Na.	M = K.
19·7	20·0

	Temp.		Time.		
m.	3°	$CaCl_2 : M_2CO_3 = 1 : 1$ mol.	60 mins.	76·3	80·0
n.	60	„ „	„	99·0	100·0

Difference between $CaCO_3$ produced in *m* and *n*.

M = Na.	M = K.
22·7	20·0

30. Comparing the influence of time, temperature, and mass upon

the chemical change under consideration, it appears that with equal molecules of the reacting bodies and moderate temperatures the amount of decomposition is greater the greater the time of action, until a certain point is reached short of complete decomposition, after which the equilibrium of the system is undisturbed. That increase of temperature disturbs this equilibrium and brings about the completion of the chemical change; but that the change is more rapidly completed, even without the aid of the energy added in the form of heat, by increasing the mass of one of the reacting bodies.

31. The experiments which have been now described have many points of contact with questions of general chemical theory. I have already alluded to a few of these. I should like now to gather together some of the leading facts established, and to indicate what appears to me to be their bearing upon a few points of general theory.

32. One is very ready to regard the present system of chemical notation as a final system; but such a system it certainly is not. The advantages of the system of notation now generally adopted are many. Among its disadvantages may I think be fairly classed the tendency, which is fostered by continued use of this system, to regard a knowledge of the initial and final distribution of mass as the all important data necessary for solving chemical problems. We too readily neglect to study the course of the chemical changes, the results of which we so assiduously register.

We have been taught by Harcourt and Esson, by Gladstone, and by others, to attend somewhat to the phenomena presented while a chemical system is passing from one state of stable equilibrium to another, in cases wherein all the reacting bodies remain in solution; but we must also attend to these intermediate phenomena in cases wherein solid compounds are produced.

A chemical system may probably be regarded as at all times tending to undergo change, possibly as at all times actually undergoing change. So long as the molecular decompositions and recompositions balance one another, a condition of apparent stability is maintained; but allow the decompositions to gain a little upon the recompositions, the stability is upset, and the change proceeds. I do not see how, but upon some such view as this, the fact is to be accounted for that a solution containing molecules of bismuthous chloride, water, and hydrochloric acid remains clear for some hours, but gradually becomes clouded from the formation and precipitation of bismuthyl chloride molecules; or how else are we to account for the production of conditions of stable equilibrium *before complete* decomposition of the bismuthous chloride (or calcium chloride) molecules, which conditions are again disturbed by the action of "impressed forces?"

33. It is possible, as has been shown, to assure the existence of a system of bismuthous chloride, water, and hydrochloric acid molecules, which system under other conditions is altogether unstable; but very slight causes suffice to disturb the equilibrium of the system, and when it is once disturbed the chemical change proceeds with considerable rapidity. But even after the change is started the final result is undetermined. Many forces are at work: one may gain a preponderance over the other, and thus modify the future course of the change. If comparatively large masses of one of the reacting bodies be used, we have a large number of one kind of molecules hovering round a small number of another kind of molecules; disturb the entropy of the system, and off goes the chemical change, regardless, to a great extent, of such subsidiary conditions as time and temperature. But let the masses of the reacting molecules be more nearly (chemically) equal, and then the subsidiary conditions come into play and exert most marked effects. The fact that time alone will not accomplish so great a decomposition as is brought about by increased temperature seems to find its explanation in the two principles: (1) that chemical changes are continually proceeding in every system comprising different kinds of molecules; but (2) that if any such system be withdrawn from the action of extraneous forces it will assume an apparently stable condition of equilibrium, which state is disturbed only by the action of "impressed force."

It appears to me that a study of the latter of those chemical changes, a partial analysis of which has been attempted in the present paper, under conditions where the action of the various forces might be more disentangled from one another would be advisable. Such a study I am now pursuing.

34. The fact that the amount of decomposition effected by a given mass of one of the reacting bodies is largely conditioned by the circumstances under which the decomposition proceeds appears to me to militate against the value of those "dynamical units," which have been established for a few substances by Mills, and the number of which that chemist is anxious largely to increase.

35. It is worthy of remark that the amount of chemical change is always somewhat greater when potassium carbonate than when sodium carbonate is employed, other conditions being constant.

36. I reserve the discussion of the bearing of my experiments upon the general question of chemical affinity until I am able to lay more detailed results of the influence of temperature, time, dilution, physical condition of the precipitating vessels, &c., &c., before the Society.

No. 2.—*On the Action of Aqueous Hydrochloric Acid upon Bismuthous Oxide.*

By M. M. Pattison Muir.

1. It is well known that hydrochloric acid dissolves bismuthous oxide (Bi_2O_3) with formation of bismuthous chloride, and that addition of water to this solution causes precipitation of bismuthyl chloride (BiOCl). The configurations through which the system passes before the condition of final equilibrium is attained have not, however, I think, been fully examined.

2. When preparing solutions of bismuthous oxide in aqueous hydrochloric acid for use in the experiments described in the foregoing paper, I noticed that if the oxide is gradually added to the acid a clear liquid is at first obtained, but on further addition of bismuthous oxide this liquid yields a white precipitate. A quantity of this white precipitate was collected, dried, and analysed; it consisted of pure bismuthyl chloride, BiOCl.

The equation $Bi_2O_3 + 6HCl = 2BiCl_3 + 3H_2O$ does not therefore present a complete account of the action of aqueous hydrochloric acid upon bismuthous oxide.

3. A weighed quantity of bismuthous oxide was added in small successive quantities to 21·5 c.c. of prepared acid—

(1 c.c. acid = 0·2701 gram HCl and 0·8519 gram H_2O.)

8·156 gram of the oxide was dissolved without production of any insoluble substance. A further quantity of 29·61 gram of bismuthous oxide was slowly added with constant agitation; the action of the acid was then complete, so far as could be determined by the eye alone. No bismuth remained in solution: the liquid showed a feebly acid reaction.

4. The equation $Bi_2O_3 + 6HCl = 2BiCl_3 + 3H_2O$ requires that 5·807 grams HCl (which was the amount present in the aqueous acid used) should dissolve 12·41 grams Bi_2O_3; about two-thirds of this amount, viz., 8·156 grams was actually dissolved. If, then, the bismuthous chloride be decomposed by the water present, as represented by the equation $2BiCl_3 + 2H_2O = 2BiOCl + 4HCl$, and if the acid thus formed react upon a fresh quantity of the oxide to form bismuthous chloride, which is again decomposed by the water present, it follows that the amount of HCl used should have transformed 37·23 grams of bismuthous oxide into bismuthyl chloride. The amount actually transformed was 37·7 grams, but this number is only approximate, inasmuch as the close of the reaction was determined by a rough visual method only.

5. The equation which expresses the initial and final distribution of mass, when bismuthous oxide, hydrochloric acid, and water are mixed is therefore almost certainly as follows :—

$$Bi_2O_3 + 2HCl + xH_2O = 2BiOCl + (x + 1)H_2O.$$

6. When solution of bismuthous oxide in the acid ceased the molecular proportion of the compounds present was $BiCl_3 : HCl : H_2O : = 2 : 3 : 61$. The addition of more bismuthous oxide reduces the number of hydrochloric acid molecules and increases that of bismuthyl chloride molecules, the equilibrium of the system is therefore disturbed. The hydrochloric acid present may be regarded as, in a sense, saturated; it cannot hold any more bismuthous chloride in solution; but if it were to dissolve a further small quantity of bismuthous oxide, the chloride so produced would be at once decomposed by the water present and so removed from the sphere of action. A further quantity of the oxide is therefore dissolved.

The presence of water renders possible a reaction between the hydrochloric acid and bismuthous oxide, which would not be possible but for the presence of that water.

We have here another illustration of that modifying influence exerted upon a process of chemical change by the presence of a third body, which was pointed out by Brodie so long ago as 1850 in his paper "On the Condition of certain Elements at the moment of Chemical Change" (*Phil. Trans.*, 1850).

XL.—*On the Action of Oxides on Salts.* Part II.

By Edmund J. Mills, D.Sc., F.R.S., and J. W. Pratt.

In the present part* we give an account of the action of aluminic, ferric, and stannic oxides on potassic carbonate. The weight of the carbonate was the same as in Part I of these researches, and was kept constant; the temperature was about 735°, and the time three hours.

Aluminic Oxide.

18. The samples of this oxide had been carefully freed from iron and alkali. One of the samples was denser than the other, owing to prolonged ignition; the numbers obtained with it are distinguished in the table by an asterisk. The weights m of this oxide are expressed

* For Part I, see this Journal, 1878, vol. xxxiii, p. 360.

in ordinary chemical units; that is, they are divided by $Al_2O_3 = 102{\cdot}86$. The equation to the chemical effect ϵ is—

$$\epsilon = \frac{(\alpha + \beta m)\ {\cdot}038516\ m}{R + m} = \frac{({\cdot}79830 + 1{\cdot}5416\ m)\ {\cdot}038516\ m}{R + m}$$

TABLE VII.

m.	ϵ found.	ϵ calculated.	Diff. per cent.
·0024304	·0025979	—	—
·0048609	·0035928	·0037920	+ 5·55
* ·0072914	·0046357	·0055220	+19·12
·0097219	·0092235	·0078057	−15·37
* ·0145820	·0103390	·010781	+ 4·27
·0194430	·0161680	·014842	− 8·20
·0388870	·0224290	·023383	+ 4·25
* ·0486090	·0313200	·029296	− 6·46
* ·0583310	·0280070	·028989	+ 3·51
* ·0777750	·0323220	·032757	+ 1·35
* ·0972190	·0354530	·035404	− 0·14
			Sum + 7·88

The probable error of ten determinations of $(\alpha + \beta m)$ is ·016370, or 2·00 per cent. on the chemical effect. The first experiment gives an effect somewhat higher than possible, and has not therefore been used in calculating α and β. Putting $\alpha + \beta m = 1$, the maximum value of m is ·13084; or $\frac{{\cdot}13084}{{\cdot}038516} = 3{\cdot}397\ Al_2O_3$, would be required, in our experiments, to expel CO_2 from K_2CO_3: say ($10\ Al_2O_3 : 3K_2CO_3$). The active ratio for a small value of m is ($Al_2O_3 : {\cdot}79830\ K_2CO_3$); say ($5Al_2O_3 : 4K_2CO_3$).

Ferric Oxide.

19. The oxide was very carefully purified, and then ignited for several hours. As will be evident from the numbers in the subjoined table, there are three distinct stages in the evolution of carbonic dioxide when ferric oxide acts on potassic carbonate. In the first stage, we encounter for the first time a variable factor of condition; $\alpha_1 m$ being equal to ·00039296. On the other hand, α_2 and α_3 are probably constant. We have deduced the mean value of $\alpha_1 m$ from the first three experiments only: rejecting the fourth, because it differs from the entire chain of observations,* and the fifth, on account of the smallness of α_1 at that point. We have taken $Fe_2O_3 = 160{\cdot}04$—

* The tabular values are the mean of three special determinations. If this peculiar result is not accidental, there must be some critical property depending on the action of 9 parts of ferric oxide on 1 part of carbonate.

	$\alpha_1 m$.	α_2.	α_3.
Mean	·00039296	·077445	·18161
Probable error ..	·000001	·002	·002

There is thus a noteworthy difference between ferric oxide and alumina.

TABLE VIII.

m.	ϵ found.	ϵ calculated.	Diff. per cent.	α calculated.	No.
·0015621	·0003780	·0003812	+ 0·86	·24939	i
·0031242	·0003666	·0003667	+ 0·03	·12573	ii
·0062484	·0003438	·0003407	− 0·90	·06346	iii
[·0093727]	[·0010000]	—	—	[·12992]	iv
·0124960	·0004349	—	—	·04575	v
·0156210	·0008789	·0008749	− 0·45	·077445	vi
·0187450	·0010724	·0009951	− 7·21	,,	vii
·0249930	·0012201	·0011969	− 1·90	,,	viii
·0374900	·0013456	·0014978	+11·37	,,	ix
[·0437390]	[·0031103]	—	—	[·14611]	x
·0499870	·0041120	·0041433	+ 0·76	·18161	xi
·0562360	·0042372	·0043459	+ 2·56	,,	xii
·0624840	·0046698	·0045372	− 2·84	,,	xiii
			Sum + 2·28		

Probable error per cent. of ten comparisons of ϵ, = 1·01.

Stannic Oxide.

20. This substance was prepared from very carefully purified tin, by digestion with distilled hydric nitrate, washing, and prolonged ignition. The powdered residue was very hard.

As will be seen from the numbers given below, there are three distinct stages in the action of stannic oxide on potassic carbonate. We may denote these by ϵ_1, ϵ_2, ϵ_3, successively; and to each stage of chemical effect corresponds a special coefficient (α_1, α_2, α_3). All these effects correspond with the general type—

$$\epsilon = \frac{\cdot 038516\ \alpha\ .\ m}{\mathrm{R} + m}.$$

The mean values of α and their probable errors are—

	α_1.	α_2.	α_3.
Mean	·43905	·11761	·20255
Probable error.	·005	·004	·008

The ratios of minimum active proportion change consecutively from ($9SnO_2 : 4K_2CO_3$) to ($8SnO_2 : K_2CO_3$), and finally to ($5SnO_2 : K_2CO_3$). There is thus a transition from decreased to increased activity on the

part of the stannic oxide, the ultimate effect being such as to produce potassic metastannate, $K_2O.5SnO_2$.

We have taken $SnO_2 = 150{\cdot}00$.

TABLE IX.

m.	ϵ found.	ϵ calculated.	Diff. per cent.	α calculated.
·0016628	·00069672	·00071219	+ 2·22	·43905
·0033333	·00141390	·0013940	− 1·41	,,
·0066666	·00067395	·00067849	+ 0·67	·11761
·0133332	·00137970	·0011967	−13·26	,,
·0266664	·0016757	·0019021	+13·51	,,
·0400000	·00231320	·0023778	+ 2·79	,,
·0533328	·00493160	·0047870	− 2·93	·20255
·0666666	·00551220	·0052181	− 5·33	,,
·0799999	·00601320	·0055475	− 7·74	,,
·1000000	·00484150	·0058361	+20·54	,,
			Sum + 9·06	

Remarks.

21. The experimental results are comprised in the following table:—

TABLE X.

Oxide.	Condition.	Units of oxide required to expel CO_2 from K_2CO_3.
Aluminic	735°	3·40
Ferric	,,	(1) 0·00, nearly.
,, ...	,,	(2) 2·01
,, ...	,,	(3) 4·72
Stannic	,,	(1) 11·19
,, ...	,,	(2) 3·05
,, ...	,,	(3) 5·26

22. It is evident from what has been stated with regard to alumina, that of the different oxides we have hitherto examined, it most closely resembles silica, the principal index of this resemblance being the increase of the value of its "factor of chemical effect" with the mass m of the oxide, according to a law $(\alpha + \beta m)$. The maximum value, however, of m is 21·63 for silica, or about six times its amount in the case of alumina: alumina is thus more acid than silica towards potassic carbonate.

23. Our anticipation that ferric oxide would resemble alumina,

failed wholly to be realised. From 2·4 grams of ferric oxide downwards, the factor of chemical effect increases as the mass of oxide diminishes, and should become infinite when m is very small. The peculiar action of small quantities, as, for example, of hydric sulphate in etherification, and the decomposition of nitrates by hydric sulphite in presence of a trace of iron salt, is here quantified for the first time.

After a certain stage, ferric oxide acquires a new kind of activity, its factor now remaining constant for considerable additions of oxide; and this stage is followed, with some abruptness, by another, in which a new factor remains constant. [Some indication of continuity between these two stages is shown in Table VIII, Expt. x.]

24. The history of the action of stannic oxide closely resembles that of ferric oxide in the two later stages; stannic oxide, however, having three consecutive hyperbolas, with three constant values of its factor. The final effect of this oxide is to produce an approximation to metastannate, as it clearly ought to do.

25. In searching for analogues of these remarkable changes, we have been led to the conclusion that the "action of oxides on salts" is a case of cumulative resolution (*Philosophical Magazine*, June, 1877, Supplement), and Watts's Dictionary, 3rd Supplement, p. 593). Consider, for example, the case of cannose, when, under the influence of heat, it is made to yield the series of caramels—

$$n\mathrm{C_{12}X_{11}}^{*} - (n-1)\mathrm{X} = \mathrm{C_{12}}n\mathrm{Y_{10}}n+1.$$

The ratio r is $\frac{11n}{10n+1}$; and the caramel becomes $n\mathrm{C_{12}X_{10}}$ when n is infinite. The body $\mathrm{C_{12}X_{10}}$ in its turn undergoes a similar decomposition, so that we get—

$$r_2 = \frac{11n}{9n+1},$$

etc. etc.

or, in general—

$$r_p = \frac{11n}{(11-p)n+1}.$$

Now, in this expression, r_p, when viewed kinetically, evidently represents the effect of the dehydrating process in the composition of cannose, and is therefore the e of our oxide equations: $(11-p)n$ is the residue of $\mathrm{X_{11}}$, or our R: and 1, the mass of X ideally acting on $\mathrm{X_{11}}$ from the outset, is the m in our equations. The factor of condition for $\mathrm{X_{11}}$ is of course unity in this case; and there are ten consecutive hyperbolas, thus—

* $\mathrm{X} = \mathrm{H_2O}$.

$r_p = \frac{11n.1.1}{(11-p)n+1}$ is strictly analogous to $\epsilon = \frac{\cdot 038516.m.\alpha}{R+m}$.

The gradual exhaustion, therefore, of the CO_2 of K_2CO_3 is found to correspond with the gradual exhaustion of the H_2O of $C_{12}(H_2O)_{11}$, and many similar depletions.*

26. Work at high temperatures is necessarily liable to considerable error for individual experiments. In order to form a judgment as to how far our theory may be trusted, we have compared ϵ calculated with ϵ found, and summed the differences per cent.; the probable error per cent. of all the determinations, and of a single determination, has also been ascertained. The results are—

	Table.	No. of determinations.	Probable error per cent. of n determinations.	Probable error per cent. of one determination.
Tungstic oxide ..	I	8	0·15	0·44
Silicic „ ..	II	9	0·59	1·77
„ „ ..	III	6	0·92	2·25
„ „ ..	IV	7	0·50	1·33
Titanic „ ..	V	8	1·20	3·39
Aluminic „ ..	VII	10	2·00	6·33
Ferric „ ..	VIII	10	1·01	3·19
Stannic „ ..	IX	10	2·12	6·70
		Mean	1·06	Mean 3·18

So far, then, as the work has hitherto extended, it is fairly represented by the simple theory we have applied to it.

XLI.—*On the Determination of Tartaric Acid in Lees and Inferior Argol, with some Remarks on Filtration and Precipitation.*

By Beaumont J. Grosjean.
(J. B. Lawes's Chemical Works, Millwall, E.)

I may perhaps be allowed to remind the Society that "lees" is the name given to the deposit which falls on the bottom of fermenting wine-vats. It consists of calcium tartrate and potassium bitartrate in variable proportions, together with large quantities of fermentative

* Between stages (1) and (2) in the decomposition of the carbonate by stannic oxide, there should be four hyperbolas of the same length as between (2) and (3). Some indications of their existence is visible in the experimental numbers; but a proof of it would require a most minute and laborious investigation.

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matters. It also contains phosphoric acid, iron, alumina, &c. "Argol" is the crystalline crust which forms on the sides of the vats. It contains much less impurity than lees. "Tartar" is the result of a process of crude refining which is applied to argol and lees. Argol is also used loosely as a synonym for both lees and tartar.

All these substances are sold to the makers of tartaric acid, and the value of them was, till lately, determined by various indirect processes, some of them very tedious, and all of them unsatisfactory in the case of lees and inferior argol.

No direct method existed for the determination of tartaric acid in lees, argol, and tartar, until my friend and predecessor, Mr. Warington, published his "Oxalate Method" (*Chem. Soc. J.* [2], **13**, 973).

This method, with individual variations, is, I believe, now exclusively employed in fixing the value of lees and inferior argol sold in the London market. Tartar, if good, gives by the indirect methods, C and D, described on p. 959 of the above-named paper, the same result as by the direct oxalate method; one of these indirect methods is, therefore, always employed in our laboratory for tartar, since the indirect methods referred to are shorter than the direct and involve less manipulation.

By the direct oxalate method, as originally described, the sample of lees or argol, very finely ground, is treated with a little water and heated to 100° C. An excess of neutral potassium oxalate is then added, and, after the mixture has been digested for a quarter of an hour, the free acidity is nearly neutralised with caustic potash. After a short further digestion, with frequent stirring, the whole is transferred to a vacuum-filter and the residue washed. The filtrate and washings are then suitably concentrated; they contain all the tartaric acid of the substance employed, in the form of neutral potassium tartrate; an excess of citric acid is then added, and the tartaric acid is by this means precipitated as potassium bitartrate. The precipitate is collected and washed, and the amount of tartaric acid is finally determined by titrating the washed precipitate with standard alkali.

Having had four years' experience of this method, I think it will be useful if I state the way in which I have found it best to work with it. I will take each step in the process, as summarised above, and describe the experiments I have made in connection with it. I will also state a few points of interest in general analysis which have arisen in the course of this investigation.

I. *Treatment with Potassium Oxalate.*

This operation, which has given to the method its name, involves a rough idea of the amount of lime present. This is necessary in order

to calculate the quantity of potassium oxalate required. The amount of lime is determined with sufficient accuracy as follows:—The acidity of 5—10 grams of the sample is first determined by treatment with a dilute solution of caustic soda. (By this means an *approximate* indication of the amount of bitartrate present is obtained.) The neutralised mixture is then boiled for half an hour with sufficient potassium oxalate to leave an excess of at least 1½ gram of that salt. It does not matter how much greater than this the excess may be, but the work will probably be increased by adding a very large quantity. The next step is to determine the amount of excess by cautious addition of standard solution of calcium chloride, each addition being followed by filtration of a small quantity of the liquid for the purpose of seeing whether a precipitate is formed on adding some of the test solution. A standard solution of potassium oxalate is also employed in a similar way when the calcium chloride fails to give any indication of excess of soluble oxalate. Acetic acid should be present in order to keep up calcium tartrate. When neither calcium chloride nor potassium oxalate causes any precipitate, or but a small one, the quantities of chloride and oxalate employed are noted. From the total oxalate employed is subtracted the amount equivalent to the calcium chloride added. The remainder is the oxalate equivalent to the lime in the substance.

A fresh portion of the sample is now taken. It should contain about 2 grams of tartaric acid. This is approximately ascertained either by experience of the kind of sample or by a previous trial by an indirect method, the one I can most recommend being that called C on p. 959 of Mr. Warington's paper. The result by this method in the case of lees generally stands to that obtained by the oxalate method as 100 to 85. I have, however, known instances where it was 100 : 50 and even 100 : 33, showing how necessary a direct method is for lees.

The substance is softened with water, and so much neutral potassium oxalate is added as the testing which has been just described indicates as the equivalent of the lime. An excess of about 1½ gram of oxalate is added to ensure the decomposition of the calcium tartrate. The solution of potassium oxalate which I employ contains 25 per cent. of the crystallised salt.

II. *Neutralisation with Caustic Potash.*

When the above mixture has been digested for a few minutes in a water-bath at 100° C. the acidity, if any, is *nearly* neutralised by addition of caustic potash. The strength of my solution of potash is 3·5 per cent.; the amount required is calculated from the quantity of standard

alkali used in determining the acidity of the sample. The potash must be added drop by drop to the hot mixture, with constant stirring, in such a way that the alkali is never in excess, otherwise colouring matter may be dissolved and be subsequently precipitated with the bitartrate. If the alkali should accidentally be added in excess, then hydrochloric acid should be added in decided excess, and not merely to simple neutrality; the addition of potash is then repeated until the solution is only very slightly acid.

Some samples of lees exhibit no indication of bitartrate after digestion with the oxalate. In fact, the addition of the oxalate in these cases produces an *alkaline* reaction from the conversion of calcium carbonate into oxalate with formation of potassium carbonate. In this case it is best to add hydrochloric acid in excess in order to decompose the carbonate, and then to nearly neutralise the free acid.

The mixture thus nearly neutralised is digested at 100° C. for half an hour, with frequent stirring. It is then ready for filtration.

III. *Filtration from the Residue.*

The neutralised liquid, which should have a bulk of not more than 30 c.c., is then separated from the residue of calcium oxalate, vegetal matter, &c., by means of a vacuum-filter. The solution generally passes more quickly if it is filtered hot. I employ for this purpose the filter described by Casamajor (*Chem. News*, **32**, 45), with an improvement to be presently mentioned. Casamajor's filter consists of a flat metallic disc pierced with small holes. Upon the disc is placed a flat circle of filter paper having a diameter about 5 mm. greater than that of the disc. The disc is placed in a funnel which, it is stated by Casamajor, must be shaped somewhat like a thistle-funnel or wine-glass, the sides forming an angle of not less than 165° with the upper side of the disc, so that the deformation of the paper may be reduced to a minimum. This supposed necessity for a funnel of a particular shape has, no doubt, been an obstacle to the use of this filter, but I find that an ordinary funnel will do just as well with care. The paper is moistened with water and pressed down flat with the aid of the vacuum. The operation takes but a few seconds, and when once the paper is covered by a precipitate no air-channels can be formed between the glass and the paper, such as frequently take place with Bunsen's filter. Casamajor's filter has the advantage that all the water must go through the residue, whereas in the ordinary filter a great part flows away uselessly down the sides. Then, again, this kind of filter, besides other advantages described by Casamajor, requires very little paper, a disc of 30 mm. in diameter being quite enough for the filtration of the residue in the present case, and

indeed for all ordinary purposes. The separation of the residue from the paper, if required, is very much easier than with Bunsen's filter. It might be thought that the paper would form folds, especially with a conical funnel, through which the residue would pass. This is not the case, however; the folds are indeed formed, but they are kept quite flat by the pressure, so that none of the residue passes through them. The disc may of course be made of several materials. I employ discs of platinum, of lead, and of pumice. Unless the disc is thin, its edge should be bevelled to fit the glass. In filtering lees, a layer of roughly ground pumice should be placed on the paper before the filtration. The pumice should be previously kept for some time in boiling water in order to free it from air, otherwise it floats on the surface of the liquid in the filter, and, mixing with the residue, forms air-channels in it when the liquid has drained through. This layer of pumice will be found unnecessary with argol. Its use greatly diminishes the time required for filtering from the residue in the case of lees.

With some very impure lees, the liquid passes too slowly to be convenient, even with the aid of the pumice. In this case an improvement is sometimes effected by allowing the first running to pass through and then transferring the residue to a new filter. The rest of the liquid and the washings will then pass more quickly; partly, perhaps, because the fine particles are now so associated with the coarser, that the paper does not get clogged up (see page 350); and, partly, because the partial drying of gelatinous matter has caused it to shrink.

An important point, and one which applies to other substances besides the one under consideration, is the way in which filtration is conducted on a vacuum-filter. The usual mode of filtration on a vacuum-filter is to drain all the liquid away and then to press the residue together to prevent it from cracking. The residue, in the case of lees, when thus pressed, becomes very impenetrable indeed. The washing of this pressed residue formerly took me several hours. But the filtration and washing required for about 10 grams of lees may generally be finished within half an hour by watching for the instant when the surface presents no visible moisture, and then immediately putting on a fresh washing, before the residue cracks, without any pressure whatever beyond that furnished by the vacuum.

Jago (*Chem. News*, **33**, 54) tried Casamajor's filter, attributing its invention, however, to Carmichael, who, indeed, proposed an apparatus on the same principle, but one which would be very difficult to make. Jago concluded that Casamajor's filter was very liable to get clogged with, *e.g.*, ferric hydrate, so that after a very short time the filtration ceased almost entirely. But I find that ferric hydrate may be washed on this filter, even when Swedish paper is used, provided no

other pressure is put on the hydrate than the gentle pressure of the air indicated by 250 mm. of mercury, and the droppings pass at the rate of 20 drops per minute. It is true this is not very fast, but it is certainly not a complete cessation. I think the better results which Jago obtained with the ordinary Bunsen's filter were due partly to the larger surface of drainage in using that filter, and also to the fact that perhaps some of the water passes down the sides in the manner before referred to.

A little more water is employed in using the method of washing which I have described, but it will be found to save much time, even if the filtrate should require evaporation in consequence of the extra water used. But no evaporation will be needed with lees, if the proportions given at the beginning of this section are followed. Ten washings of 2 or 3 c.c. each will be found to be enough to wash out the potassium tartrate, and the vol. of the filtrate and washings will then equal 50 c.c. Very little vacuum is required for this purpose; a pressure represented by 250—350 mm. of mercury being quite sufficient. The residue may be pressed after the last washing has gone through.

The following experiment confirms the statement as to the amount of washing which is required in the case of lees.

1·9877 gram of tartaric acid in the form of neutral potassium tartrate was dissolved in 30 c.c. of water, and the solution was thoroughly mixed with the residue left from 10 grams of lees from which all the tartaric acid had been carefully removed. The mixture was filtered on the vacuum-filter, and washed with 10 washings of about 3 c.c. each. Tartaric acid was determined in the filtrate, which had a vol. of 50 c.c., in the way to be described presently as giving the best results. I obtained 1·9815 gram of tartaric acid, or 99·7 per cent. of the quantity taken. Another experiment showed that 95 per cent. is got out by only three washings. But I always wash ten times for the sake of safety. If the filtrate and washings should, however, by chance amount to 48 c.c. before the analyst is satisfied that all the tartaric acid is washed out, then any farther washings must be collected separately, concentrated by themselves to 1 or 2 c.c. and added to the bulk, which must not exceed 50 c.c. (see Mr. Warington's paper, p. 973).*

Sometimes a sample is met with which filters at an extremely slow rate, even when the residue is transferred to a fresh filter. In such a case I resort to a method which was suggested to me by a friend. This method consists in taking a larger quantity of lees for

* I wish it to be understood that I claim no credit for the principle of the filter described above; the credit of it belongs to Casamajor, but I think he will not object to my thus bearing witness to its usefulness, and extending that usefulness by showing that an ordinary funnel may be employed.

analysis, and, after decomposition with oxalate and neutralisation with potash, making the whole up to a known volume with such a quantity of water, that the solution of potassium tartrate shall not be too dilute for the purposes of the oxalate method. The residue is then allowed to settle down. Meanwhile, the space occupied by the residue is determined as follows :—Another portion of the sample is also decomposed with oxalate and neutralised. It is then drained on a coarse filter, but not washed. The residue is removed, dried over steam, ground finely, and then dried at 100° C. It will be found that the residue from lees is very easily ground at that point when it is just free from visible moisture, but if it be allowed to dry farther it becomes very tough and difficult to grind. The residue is finally placed in a graduated cylinder, mixed with a known volume of water, and left to absorb all the water possible. The volume of the mixture is then read off, and this, *minus* the volume of the water taken, gives the volume of the residue. Returning to the first quantity of lees taken, and now knowing how much of it is residue and, therefore, how much is solution, we can take a proper proportion of the clear liquid for the determination. The following example shows that this method, though much longer than the filtration method, and only to be employed when the latter is inapplicable, gives results sufficiently near those given by filtration. In this instance I employed a sample which could also be treated by the filtration method in order that the results of the two methods might be compared.

10 grams of lees were decomposed with potassium oxalate and neutralised. The mixture was allowed to get quite cold and filtered on a canvas filter. It is unnecessary to wash this residue, since the small quantity of soluble salts remaining can make no appreciable difference in the determination of the volume of the residue. The residue was then dried over steam, ground finely, and dried at 100° C. It was then placed in a graduated cylinder, 50 c.c. of water were added, and the whole left for some hours. The water, *plus* the residue, then occupied a space of 53·75 c.c.; therefore the residue from 10 grams of lees = (53·75 — 50) = 3·75 c.c. in volume.

Meanwhile, 35 grams of the lees had been decomposed with oxalate and neutralised with potash, the vol. of the mixture being throughout these operations as nearly as possible three and a half times as great as in the similar operations with 10 grams. When the liquid was quite cold the whole was made up to 250 c.c., allowed to settle, and 50 c.c. of the clear liquid taken into a beaker. From the experiment with 10 grams it will be seen that the 250 c.c. were made up of (0·375 × 35) = 13·1 c.c. of residue, and (250 — 13·1) = 236·9 c.c. of solution. Consequently, 50 c.c. contain the tartaric acid from $\left(\frac{50}{236{\cdot}9} \times 35\right)$ = 7·3871 grams of lees.

The 50 c.c. of liquid gave, on precipitation with citric acid, &c., as described farther on, bitartrate equivalent to 1·9753 gram of tartaric acid, or 26·7 for 100 of lees.

I then determined tartaric acid in 7·3871 grams of the lees, employing the vacuum-filter to separate the residue. I obtained bitartrate equivalent to 1·9362 gram of tartaric acid, or 26·2 for 100 of lees. Thus the two methods differed by 0·5 per cent., *calculated on the lees*, which would be rather too great a difference, were it not that the kind of lees to which I apply this method is almost worthless.

And here I may say that I find that if I take equal quantities of washed potassium bitartrate, as obtained in the oxalate process, and titrate with caustic soda, the quantity of soda required in any one case is within 0·5 per cent. of the average amount required. This is an unavoidable variation, and it is also, I think, the only allowable one in the method. I therefore consider that two analyses agree, or that a test experiment is satisfactory, if the results do not differ by more than 0·5 per cent. of the tartaric acid taken.

Whether the liquid be separated from the residue by filtration, or by subsidence, we have now obtained all the tartaric acid contained in the substance taken in the form of neutral potassium tartrate, excepting a trace, purposely left, in the form of bitartrate.

IV. *Addition of Potassium Chloride.*

The liquid, which must be quite cold, is now treated with potassium chloride. This addition, which is a new feature in the analysis, is founded upon the observation of Mr. Warington that potassium chloride reduces the solubility of potassium bitartrate. He found that a cold solution of the chloride containing 3·72 per cent. dissolved 1 in 2,981. But a 10 per cent. solution has still less solvent power, as shown in the following series of experiments I have made:—

Water at 12° C. dissolved.....	1 in	262
5 per cent. KCl solution at 12° C.	1 in	3,213
10 „ „ „	1 in	4,401

I therefore add 5 grams of potassium chloride to the 50 c.c. of solution of neutral potassium tartrate which have been obtained as described in Section III. This has the effect of making the subsequent precipitation of the bitartrate more complete than would otherwise be the case. The liquid is stirred till the chloride is dissolved, and is then ready for precipitation.

V. *Quantity of Citric Acid required.*

To ensure the precipitation of all the tartaric acid, the quantity of

citric acid added must be 1—1·5 gram in excess of that required by the equation—

$$3K_2\bar{T} + H_3\bar{C}i.aq. = 3KH\bar{T} + K_3\bar{C}i.aq.$$

That is to say, if 2 grams of tartaric acid are contained in the quantity of substance employed, then 2—2·5 grams of citric acid are to be taken. This is proved by the following experiments:—

1·9877 gram of tartaric acid, in the form of neutral potassium tartrate, was dissolved in 50 c.c. of water containing 5 grams of potassium chloride. Three solutions, thus prepared, were precipitated with the following quantities of citric acid:—

I.	1·5 grams	=	0·6 gram	in	excess.
II.	2·0 „	=	1·1	„	„
III.	2·5 „	=	1·6	„	„

The precipitates were treated as described hereafter, and were equivalent to the following quantities of tartaric acid:—

I.	1·8950 grams	=	95·3	for	100 taken.
II.	1·9712 „	=	99·2	„	„
III.	1·9856 „	=	99·9	„	„

The same results were obtained when the usual conditions were more closely imitated by adding $1\frac{1}{2}$ gram of neutral potassium oxalate before precipitation.

If, therefore, the quantity of bitartrate finally obtained, in this method of determining tartaric acid in lees, shows that insufficient citric acid was used, the analysis should be repeated, using the proper proportions.

VI. *Mode of Precipitating the Bitartrate.*

The citric acid may be added either in the solid state or in a strong solution; one containing 50 per cent. of the acid will be found convenient.

If the acid solution be gently mixed with the liquid, and the whole be then left undisturbed for several hours, the precipitate comes down in well-defined crystals. If, on the other hand, the mixture be stirred for a few minutes, the bitartrate comes down in the form of very minute granular crystals. In starting with perfectly cold solutions, the final result is the same in both cases after several hours (I cannot speak with certainty of the exact length of time required, but it is less than 18 hours). This is shown by the following experiment.

Two solutions, each containing 2·0214 grams of tartaric acid in the form of neutral potassium tartrate, and having a volume of 50 c.c. (temperature 13° C.), were treated with 2·5 grams of citric acid in solution. No. 1 was stirred, after adding the acid, *continuously* for 10 minutes.

No. 2 was simply mixed, by shaking the beaker round a few times. Both solutions were left all night. They were then treated with 5 grams of potassium chloride (see Section IV), and after an hour they were filtered, the precipitates washed in the usual manner, and tartaric acid determined in them. They both gave 2·0101 grams of tartaric acid, or 99·5 per cent. of that taken.

If, with the view of making the larger crystals as large as possible, the mixture be *warmed* and allowed to cool very gradually, supersaturation takes place, and the slow precipitation gives too low a result, as proved by the following experiment.

Two solutions, each containing 1·9963 gram of tartaric acid in the form of potassium tartrate, and having a volume of 50 c.c., were treated with 2·5 grams of citric acid. No. 1 was stirred continuously for 10 minutes after adding the acid. No. 2 was made hot and treated, while hot, with the citric acid. It was then allowed to cool slowly. The next day, to both solutions were added 5 grams of potassium chloride, and the precipitates treated as usual. The tartaric acid obtained in the form of potassium bitartrate was as follows:—

I. 2·0025 = 100·3 for 100 taken.
II. 1·9243 = 96·4 „ „

The precipitation in large crystals compares unfavourably with the granular precipitation as to the time required; for, as will be shown presently, the granular precipitate requires but a few minutes for completion, whereas the slow precipitation scarcely commences in the same period. In fact, the only advantage of the large crystals is in the fact that large crystals generally wash more easily than small crystals. But, in many cases, I have found even this advantage to be lost, and the larger crystals to take longer in washing. The reason of this seems to be that one cannot always ensure that a liquid shall contain no solid matter but large crystals; a very minute proportion of finely divided matter will sometimes be present; of no consequence, indeed, as affecting the final result of the analysis, but of great consequence as affecting the rate of filtration. For, in such cases, the finely divided matter is all thrown upon the paper, the pores of which are thereby stopped up. Thus, though the crystals themselves may be washed easily enough, the washing fluid passes but slowly through the paper. But if the substance to be washed be in the form of very small crystals, it is so associated with the finely divided matter, that it keeps it from the paper. As an example of this, I may mention that aluminium phosphate, by itself, is very difficult indeed to wash, but if it be formed in the presence of sulphur, as in Esilman's method of separating alumina from iron, it may be filtered and washed readily. I have also found aluminium phosphate to filter very well if calcium oxalate

or sulphate be precipitated along with it. The bitartrate should, therefore, always be precipitated in the granular state.

I confirm the remark of Mr. Warington, that there is no reason to fear that potassium binoxalate will come down with the bitartrate if the proportions given in Section I are adhered to, viz., to have only about $1\frac{1}{2}$ gram of potassium oxalate in excess. This is shown by the following experiment.

I employed 50 c.c. of a solution containing as much as 7·3 grams of crystallised potassium oxalate, together with 1·5 gram of neutral potassium citrate and 5 grams of potassium chloride (to imitate the usual conditions). To this mixture was added 1·5 gram of citric acid, the usual excess. No precipitate was visible after standing all night.

In another case in which the potassium oxalate was increased to 8·8 grams, only one small crystal of potassium binoxalate appeared after leaving the mixture all night. The temperature at the time of these experiments was never above 11° C., and at night was below it.

But, nevertheless, the excess of oxalate should not be much greater than $1\frac{1}{2}$ gram, for it then tends to prevent the precipitation of bitartrate. And again, the binoxalate, if precipitated, although it is easily soluble in the washing fluid, causes the latter to become more acid, and thus to dissolve more bitartrate.

VII. *Length of Time required for the Precipitation of the Bitartrate.*

The precipitating solutions were formerly left 12 hours to ensure complete precipitation. But I was surprised to find, and I think others will share that surprise, that the bitartrate is completely precipitated by *stirring continuously for only* 10 *minutes*. This is shown by the following experiment.

Two grams of tartaric acid, in the form of neutral potassium tartrate, dissolved in 50 c.c. of water, were treated with 5 grams of potassium chloride and a solution of 2·5 grams of citric acid in 5 c.c. of water. The whole was stirred continuously for 10 minutes. Temperature after precipitation = 16° C. The precipitate was then immediately filtered, washed, and treated as usual. It was equivalent to 1·9918 gram of tartaric acid, or 99·6 per cent. of the quantity taken.

But, for the sake of safety, I always wait for half an hour, after this continuous stirring, before filtration. If this interval be allowed to elapse, the temperature may, with perfect safety, be even higher than in the last experiment. Thus, in the case of a sample of lees, the solution was stirred continuously for 10 minutes with the acid, and then left for half an hour. Temperature = 21·5° C. The precipitate was then filtered off at once, and the filtrate left all night. The next day there was a mere trace of precipitate in the filtrate; in fact, on collection, washing, &c., it was equivalent to only 0·004 gram of

tartaric acid, or about 0·2 per cent. of the whole quantity originally taken.

This rapid precipitation of bitartrate is also applicable to Mr. Warington's method of determining the real tartaric acid in the liquors of a tartaric factory (p. 977 of his paper), at least when the bitartrate is formed in the presence of the same proportion of the other products of reaction as in the cases I have mentioned. The method depends, it will be remembered, on the following reaction:—

$$K_3\bar{C}i.aq. + 3H_2\bar{T} = 3KH\bar{T} + H_3\bar{C}i.aq.$$

and, since an excess of potassium citrate is used, the three products of the reaction are the same, in kind, as in determining tartaric acid in lees. It is true that, in most liquors of a factory, there is a variable quantity of sulphuric acid, which acts upon the potassium citrate, thus:—

$$2K_3\bar{C}i + 3H_2SO_4 = 3K_2SO_4 + 2H_3\bar{C}i.$$

A variable proportion of citric acid is thus introduced, which exerts a certain, though not generally a large, dissolving power on the bitartrate. But I now eliminate this source of variation by completely neutralising the liquor with potash, allowing the potassium sulphate to crystallise out, if it is large in quantity, and precipitating the neutral solution with the proper quantity of citric acid. Another advantage of this last method is that many factory liquors contain large quantities of aluminium and iron phosphate, which are more or less perfectly precipitated when the liquid is diluted, neutralised by potash and heated, as may be gathered from the conclusion of Mr. Warington's paper. These impurities can thus be in part removed before precipitating the tartaric acid. A still better way of performing this operation is to completely precipitate the liquor with whiting, and then to boil with excess of potassium oxalate. By this means, the aluminium phosphate, &c., is obtained mixed with calcium oxalate, and filters pretty well, while by the first process it filters very slowly. Moreover, by the first process loss of tartaric acid might occur if gypsum were present, but not so by this method.

The experiment which I made to see if the tartaric acid could be thus precipitated in 10 minutes, was made, however, before I had adopted the plan just mentioned. The variation of the quantity of citric acid due to the second equation was got rid of by having no sulphuric acid present. Two equal quantities of crude tartaric acid were dissolved in equal volumes of water, and precipitated with equal quantities of potassium citrate. No. 1 was stirred continuously for 10 minutes, then immediately filtered, and treated as usual. No. 2 was stirred

and left all night, then filtered, &c. The precipitates were equivalent to the following quantities of tartaric acid:—

No. 1. 1·6572 gram.
No. 2. 1·6672 „
Taking No. 2 as 100, No. 1 = 99·4.

When citric acid is added to a solution of neutral potassium tartrate, a rise of temperature takes place. But this does not amount to 2° C. in the usual conditions. Since I have shown above that the temperature *after* precipitation may safely be 21·5 C., it is evident that the temperature *before* precipitation may be about 19° C.

The discovery of the rapid precipitation of bitartrate, coupled with that of the quickness with which the residue may be washed (Section III), greatly reduces the time required for this determination, which formerly took a day and a-half, but can now be performed *in four hours.* (See summary at end of paper.)

There are other cases in general analysis, in which it is the custom to "allow the substance to stand 12 hours before filtration." It is possible that a few experiments would show that in many cases this is quite unnecessary, and that agitation may be substituted for long standing.

VIII. *Filtration and Washing of the Bitartrate.*

The bitartrate should always be filtered and washed on the vacuum-filter, in the case of lees. If, however, the bitartrate has been precipitated from a solution obtained by subsidence of the residue (Section III) it may contain finely divided matter, which hinders it from filtering well on the vacuum-filter. In such cases it should be drained and pressed, and then dried for some time on the vacuum-filter by the current of air. If it is then transferred to a new filter with a little of the washing fluid, it may be washed with ease.

The bitartrate is washed with a 5 per cent. solution of potassium chloride saturated with potassium bitartrate. Care must be taken that the chloride solution is exactly at the temperature of the air before saturating it with the bitartrate. If it be employed as a washing solution at a temperature *higher* than that at which it was saturated, it will, of course, dissolve bitartrate off the filter. If the saturation be made at a high temperature, and the solution then used at a low one, it may deposit bitartrate on the filter. If the washing solution be prepared by warming the chloride solution with excess of bitartrate, and then letting it cool to the temperature of the air, it is apt to become supersaturated. The solution should, therefore, be freshly made in every case, especially as it would be liable to decom-

position, even if the temperature did not vary. The analyst should satisfy himself that the solution is really saturated by an actual trial of its acidity. For this purpose the excess of bitartrate is filtered off through Swedish paper, since I have found that both German and English paper is apt to contain basic substances, which partially neutralise the solution. Not less than 10 c.c. of the filtered solution is taken for trial with very dilute alkali.

The bitartrate from the lees is now to be washed with the solution thus prepared. If the temperature of the air should rise during the washing, the solution must be re-saturated at that temperature before proceeding. The bitartrate must be washed free from citric acid, *i.e.*, until the drainage water has the same acidity as the washing solution. This is ascertained by taking 10 c.c. of the drainage water, and determining its acidity. It is advisable not to press the bitartrate on the filter until the conclusion of the washing.

The washed bitartrate is then pressed into a firm cake, in which condition it is readily removed from Casamajor's filter, and is transferred while still wet, with its paper, to a beaker, and titrated with caustic soda. If the bitartrate has been obtained by granulation the titration can be made without heating. But the large crystals require very careful heating with the alkali to prevent loss. The acidity of the portion of washing solution which is left adhering to the precipitate is quite infinitesimal, and may be neglected, indeed could not be estimated (see solubility of $KH\overline{T}$ in KCl solution, Section IV). The point of neutrality is best estimated by delicate litmus paper (Mr. Warington's paper, p. 927), since the bitartrate contains a small quantity of colouring matter, which masks the final tint with litmus solution.

Instead of direct titration the precipitate may be dried, ignited, the ash boiled with standard acid, and the excess of acid then determined. This will, however, take much longer than the direct titration.

IX. *Degree of accuracy attainable by the Method.*

Several test experiments described in the preceding pages have shown that the whole of the tartaric acid taken is practically recovered, when neutral potassium tartrate is precipitated as there described, the minute losses being quite within allowable limits. Two other similar experiments may here be mentioned, to show that the presence of a moderate amount of potassium oxalate or of alum produces no appreciable effect.

I. Materials:—1·9963 gram tartaric acid as $K_2\overline{T}$ + 1·6 gram $K_2C_2O_4 2aq.$ treated as usual, gave $KH\overline{T}$ equal to 2·0025 grams tartaric acid, or 100·3 for 100 taken.

II. Materials:—Same tartaric acid + ·5 gram potash alum (the acidity of which was neutralised). Obtained $KH\bar{T} = 1{\cdot}9840$ tartaric acid = 99·4 for 100 taken.

I will now give two test experiments in which the whole course of the method as applied to lees and argol, was followed.

I. I employed pure calcium tartrate, containing 2·0247 grams of tartaric acid (ascertained by ignition, solution of the ash in standard acid, and determination of the excess of acid). The tartrate was digested with a solution of 4·8 grams of potassium oxalate at 100° C. for half an hour. The mixture was then filtered and washed. The filtrate (50 c.c.) was treated with 5 grams of potassium chloride, and the whole stirred for a few minutes with a solution of 2·5 grams of citric acid in 5 c.c. of water. The precipitate was in this case left all night for convenience, but this was not necessary. It was then collected and washed with a 5 per cent. solution of potassium chloride, which had been saturated with bitartrate. The precipitate was then titrated, and was found to be equivalent to 2·0164 grams of tartaric acid, or 99·6 per cent. of the quantity taken, which is within the limits of allowable error.

II. The following mixture was made in order to represent a sample of lees:—

Calcium sulphate.....	1·00 gram.
Spanish refining earth	1·00 ,,
Potash alum.....	0·50 ,,
Phosphoric pentoxide.....	0·05 ,,
Potassium bitartrate	1·10 ,,
Calcium tartrate	2·00 grams.

The tartaric acid contained in the last two ingredients was 2·0316 grams, as determined by the acidity of the bitartrate and the neutralising power of the ash of the calcium tartrate. The mixture was digested with 4·8 grams of neutral potassium oxalate, the free acidity neutralised with potash, and digestion continued for half an hour. The rest of the operation was similar to that described in Experiment I. The bitartrate obtained was equivalent to 2·0308 grams of tartaric acid, or 99·96 per cent. of the quantity taken.

There is, therefore, no need now to add a correction, as was formerly the case, for the solubility of the bitartrate, &c. (see Mr. Warington's paper, p. 974). This correction amounted to 0·07 gram of tartaric acid when 50 c.c. of liquid were precipitated. It was employed before the introduction of the present washing solution, and the use of potassium chloride in precipitation.

X. *Time required for the Determination of Tartaric Acid by this Method.*

The following may be taken as the average time taken up by the several stages of the method:—

I.	Determination of acidity	30	minutes.
II.	Determination of oxalate required	30	,,
III.	Digestion with oxalate and neutralisation	45	,,
IV.	Filtration from residue	30	,,
V.	Precipitation with citric acid	30	,,
VI.	Filtration and washing of bitartrate	30	,,
VII.	Titration of bitartrate	30*	,,
		225	,,

Thus the determination may be finished within four hours.

I ought, perhaps, to apologise for the length of this paper. The minute detail necessary in describing a quantitative process, and the necessity of testing every point in an analytical method, by experiments on *known* substances, must be my justification for taking up so much space in the Society's Journal.

XLII.—*On a New Class of Colouring Matters.*

By Otto N. Witt, Ph.D.

A great number of aniline dyes are obtained by the oxidation of primary amines; in fact this is the oldest method of obtaining them, and the one still most frequently in use. Mr. Perkin made his admirable discovery of mauveine by oxidising aniline with chromic acid, and all the processes known for the production of magenta, with one exception only, are based on the same principle. All endeavours to clear up the mechanism of that reaction, to elucidate the different stages of its gradual progress, have, however, failed hitherto. The beautiful researches of Otto and Emil Fischer and the interesting investigations of Dale and Schorlemmer have certainly established beyond doubt the constitutional formula of rosaniline, but they do not inform us how it is possible for a reaction so fierce and so prolonged as that which takes place in a magenta melt, to confine itself chiefly to the methyl groups present and exert but a feeble influence on the amido groups.

The fact is that this influence is not so feeble as is generally assumed. When we consider theoretically the process going on in a

* The titration may be done in the cold, and will then take only five minutes (see p. 354). A correction for any trace of carbonic acid in the soda must be made in this case.

magenta melt, we think only of the formation of rosaniline, but we do not take into consideration the 66 per cent. of base which are converted into black insoluble matter, just because their amido groups enter as much into the reaction as their methyl groups. It is the fierceness of the attack of the oxidising agent on two-thirds of the aniline which allows the remaining third to be converted into a body of the most delicate nature, and so susceptible to further oxidation as rosaniline.

I think I have shown that this reaction cannot possibly give but one final product, and that it is therefore not fit for a study of the gradual progress of oxidation of amines. Without entering upon other well known processes, which have all the same defect, I shall describe the course I adopted to study the progress of oxidation in mixtures of aromatic amines, which contain methyl and amido groups simultaneously.

I have extended my researches to the two toluidines which are easily obtainable; to ortho-, para-, and metatoluylene-diamine and xylidine; to cresols, orcine, and xylenol. I shall in this paper describe only the results which I have obtained with metatoluylene-diamine, reserving to myself the extension of my new method to the other compounds named.

If a mixture of aniline hydrochloride and metatoluylene-diamine in molecular proportions be dissolved in cold water, and oxidising agents such as ferric chloride or others in aqueous solution be added very gradually, a reaction takes place resulting in the formation of new colouring matters; but, for reasons which will presently be understood, I have abstained from the use of aniline, and substituted for it the hydrochloride of another base, containing likewise only one NH_2 group, dimethylparaphenylene-diamine,

$$\begin{array}{l} N\begin{matrix}CH_3\\CH_3\end{matrix} \\ | \\ C_6H_4 \\ | \\ NH_2 \end{array}$$

If a mixture of molecular weights of this compound and metatoluylene-diamine be treated with ferric chloride, a dark brown coloration appears at once. When sufficient of the oxidising agent has been used to eliminate four atoms of hydrogen, a large quantity of sodic acetate is added. The liquid assumes instantaneously a deep indigo coloration. The addition of salt precipitates the colouring matter, which may be obtained in a pure state by filtering and washing with water.

Dimethylparaphenylene-diamine is obtained by the reduction of

nitrosodimethyl-aniline. The reduction of the latter takes place with the greatest ease, and requires four atoms of hydrogen to every molecule of the nitroso-compound, two being used for the elimination of the oxygen, and two for the final formation of the amido-group—

$$\begin{array}{l} N\begin{matrix}CH_3\\CH_3\end{matrix} \\ | \\ C_6H_4 \\ NO \end{array} + 2H_2 = H_2O + \begin{array}{l} N\begin{matrix}CH_3\\CH_3\end{matrix} \\ | \\ C_6H_4 \\ | \\ NH_2 \end{array}$$

It seemed natural to combine both processes described, and to eliminate the two atoms of hydrogen in metatoluylene-diamine necessary for the formation of the new blue, by the one atom of oxygen contained in the nitroso-group, and thus get rid of metallic and other compounds which enter into the reaction, but not into the molecule of the final product.

This plan proved to be perfectly successful. If the aqueous solutions of metatoluylene-diamine and nitrosodimethyl-aniline hydrochloride be mixed in molecular proportions, the mixture assumes at once a deep green coloration, due to the blending of the yellow colour of the nitroso compound and the newly formed blue. The proportions used in my experiments were as follow :—

36 grams of nitrosodimethyl-aniline hydrochloride
and 24 grams of metatoluylene-diamine

were dissolved each separately in 500 c.c. of boiling water. The solutions were mixed in a crystallising dish, and allowed to cool very gradually. After from 36 to 48 hours the blue mother-liquor was poured off, when the walls of the vessel were found covered with large and well-defined crystals of the new compound, from 44 to 52 grams in weight. As a further quantity of the same substance could be obtained by precipitating the mother-liquor with salt, I have no hesitation in stating that the yield was nearly theoretical. The crystals washed several times in cold water and dried on filter-paper, and finally over sulphuric acid, were pure, and fit for analysis. The dry substance will bear heating to 120° for a short time. But in the presence of water decomposition takes place even below 100°. I have effected a recrystallisation by dissolving the substance in warm water, and speedy precipitation with a concentrated solution of sodium chloride. For my combustions I have used samples obtained by different methods.

The numbers obtained showed the substance to be—

$$C_{15}H_{16}N_4.HCl + H_2O.$$

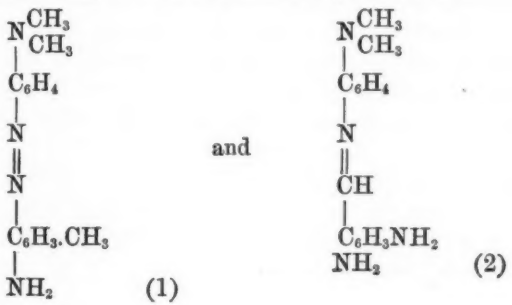
	Theory.	I.	II.	III.	IV.	V.	VI.	VII.
C 180	58·44	58·31	58·52	57·98	58·37	—	—	—
H 21	6·82	7·37	7·12	7·19	7·21	—	—	—
N 56	18·18	—	—	—	—	18·66	17·88	18·10
O 16	5·19	—	—	—	—	—	—	—
Cl 35·5	11·37	—	—	—	—	—	—	—
308·5	100·00							

That there is a molecule of water of crystallisation present may be shown by the behaviour of the substance at 150°, when it gives off one molecule of water, but it is impossible to obtain the anhydrous salt without simultaneous decomposition.

The new substance forms fine large crystals of prismatic shape, grouped in rosettes, or warty conglomerations if the crystallisation takes place very rapidly, or elongated detached leaflets if the solution contains mineral salts. Large crystals generally break up into a fine crystalline powder whilst drying under the desiccator, and the fragments show a peculiar movement when they are suddenly transferred into an atmosphere containing aqueous vapour.

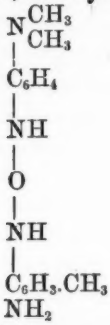
The new compound dissolves most readily in water, alcohol, and acetic acid. The solutions are of a brilliant blue when perfectly neutral. Traces of acid suffice to form a poly-acid salt of a light brown colour. Toluylene blue has this property in common with rosaniline, but shows it in a much more marked manner. If alkali or ammonia be added to the blue solution, the free base is precipitated as a tarry brown mass, which solidifies gradually, but could not be obtained in a fit state for analysis.

For the constitution of this compound two kinds of formulæ may be assumed, according to whether dehydrogenisation has taken place in one of the amido- or in the methyl-groups of toluylene-diamine. We can take it for granted that the aromatic nucleus is not attacked, because the reaction takes place at a very low temperature, and because the same reaction applied to metaphenylene-diamine results not in a similar substance homologous to toluylene blue, but in a totally different body. The two formulæ possible are—



(1) (2)

The first formula has very little probability, because it corresponds with the constitution of a true azo-body, and a near relative to chrysoïdine; and such a compound could hardly be expected to be of a blue colour. But by taking the molecule of water which so closely adheres to the substance as entering into its constitution, the formula may be altered into that of a new compound containing a chromophoric group consisting of nitrogen, oxygen, and hydrogen—



But compounds of that description, as well as a body of the constitution expressed by the first formula, would on reduction invariably split up into one molecule of toluylene-diamine and one molecule of dimethylparaphenylene-diamine, absorbing *four* atoms of hydrogen, whilst a compound of the formula 2 would in all probability absorb only two atoms of hydrogen, forming a new base. The reduction of toluylene blue takes place most easily by the action of stannous chloride. By using a standard solution of this reagent, I have been able to ascertain that only enough stannous chloride is necessary to furnish two atoms of hydrogen; if more of the reagent be added the excess remains unattacked. If after the reduction all the tin be precipitated by SH_2, and the filtered solution be evaporated to dryness, a new salt is obtained which is extremely oxidisable, and has a powerful tendency to be reconverted into the blue substance from which it was obtained. It may be easily shown that this salt is not a mixture of toluylene-diamine and dimethylparaphenylene diamine. For if it be mixed with a quantity of anhydrous sodic acetate, and the mixture treated with acetic anhydride, a new base is obtained, which on oxidation yields a violet substance similar to one obtained if toluylene blue itself be subjected to acetylation. A mixture of toluylene-diamine and dimethylparaphenylene diamine yields under the same circumstances the acetyl derivatives of these bases, one of which is a neutral compound, m. p. 219—220°, the other a base of very marked properties, crystallising extremely well, m. p. 131°, volatile without decomposition, giving a beautifully crystallised, most insoluble picrate, and a prismatic platinum double chloride.

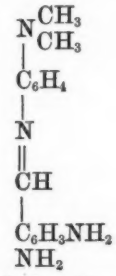
No such substance could be isolated from the product obtained by reducing the blue. Fractional crystallisation of the acetyl derivative was tried, but could not be continued, on account of the rapid oxidation. The picrate does not crystallise; the platinum salt decomposes in the moment of its formation, and the only product obtained in an attempt to distil the compound was a mass of inflated charcoal.

At last a compound was found which was fit for analysis. If the solution of the base, after precipitation with SH_2, be evaporated to syrupy consistency, and a quantity of solution of stannous chloride be added corresponding to one molecule, and if hydrochloric acid gas be then introduced at 0° until the liquid is saturated, a small quantity of impurities settles out and may be removed by filtration through glass-wool. The filtered liquid, which is almost colourless, is now mixed with an excess of stannous chloride solution. Very soon crystals begin to settle out. After several hours they should be filtered, washed with hydrochloric acid, and dried over sulphuric acid and soda-lime. The analysis gives numbers corresponding with the formula—

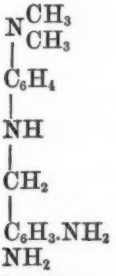
$$C_{15}H_{20}N_4.HCl + SnCl_2.$$

	Theory.		Found. I.	Found. II.
C	180	37·4	36·49	37·05
H	21	4·4	5·44	5·67
N	56	11·6	—	—
Cl....	106·5	22·0	—	—
Sn ..	118	24·6	—	—
	481·5	100·0		

These results establish beyond doubt the fact that toluylene blue does not on reduction split up into the bases from which it was derived; but that these are in its molecule, linked together in a more powerful manner than by a mere chain of nitrogen-atoms. We must therefore assume for toluylene blue and its leuco-compound, the only formulæ which fulfil this condition:—



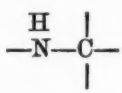
Toluylene blue.



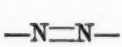
Leuco-base.

The "chromophor" in my new dye is the group—

which stands as a connecting link between the chromophors of the rosaniline—



and the azo-series—



Toluylene blue shows similarities with both series.

I have formerly proved* that certain amidoazo-compounds have so great a tendency to reduction that sometimes they may act in a manner precisely similar to an organic oxidising agent, depriving other amines of part of their hydrogen. This property is likewise, and in a most powerful degree, possessed by this new class of bodies. Whenever toluylene blue is brought into contact with another amine the blue is reduced into its leuco-compound and the other amine is dehydrogenised into a new colouring matter. Numerous new substances may be thus obtained, the simplest case being, of course, the action of toluylene blue on itself.

If a solution of toluylene blue be boiled for about twenty minutes it turns pink. After filtration from a small amount of tarry matter, it may be precipitated with alkali, and the new base purified by repeated crystallisations from alcohol. But as the leuco-base adheres tenaciously to the substance, and gradually re-oxidises into the blue, it is better to adopt another process of purification. A solution of stannous chloride is added carefully to the pink product of the ebullition of the blue. Fine crystals of the tin double salt settle out, whilst the tin double-salt of leuco-blue and all impurities remain in solution. The double-salt of the pink is filtered off, washed with dilute hydrochloric acid, and dissolved in distilled water; it is most readily soluble if no free acid be present; sufficient sulphuretted hydrogen water is added to precipitate the small amount of tin. The filtrate, on addition of an alkali, deposits bright orange needles of the new base. These needles contain four molecules of water of crystallisation, which is given off at 150—160°. The anhydrous base is of blood-red colour, and gave, when analysed, numbers corresponding with the formula $C_{15}H_{16}N_4$.

(1.) *Water of Crystallisation.*

	Theory for $C_{15}H_{16}N_4 + 4H_2O$.	Found. I.	II.
$C_{15}H_{16}N_4$.	77·8	78·19	78·25
H_2O.....	22·2	—	—

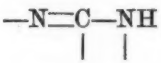
* Otto N. Witt, *Deut. Chem. Ges. Ber.*, **10**, 873.

(2.) *Combustions.*

	Theory for $C_{15}H_{16}N_4$.		Found. I.	II.	III.
C	180	71·4	71·40	71·45	—
H	16	6·4	6·78	6·94	—
N	56	22·2	—	—	22·08
	252	100·0			

This compound in its hydrated state is easily soluble in warm alcohol, with a marked fluorescence. It is very insoluble when in its anhydrous state. It forms two series of salts. The neutral salts are pink and stable; the acid salts are sky-blue, and decompose on addition of water into free acid and the neutral salt. The constitution of this compound can, according to its formation, be expressed by only one formula—

It represents another type of colouring matters containing the new chromophoric group—



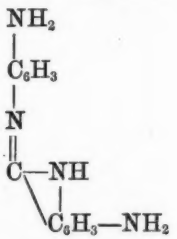
I have discovered another compound of the same class. It may be obtained by heating adequate quantities of toluylene blue and meta-toluylenediamine in an aqueous solution, acidulated with acetic acid for 12 hours to 35—40°. Its separation from the bye-products is effected by adding sulphuric acid to the mixture, and allowing to stand for 24 hours. The new compound forms a most insoluble sulphate, which, after being purified, yields the free base on decomposition with alkali. In its hydrated condition this base is a powder of a vermilion colour, soluble in alcohol, isobutyl alcohol, and ether; and exhibiting in its solution a brilliant orange fluorescence. At 130° the water is given off by the hydrated base, and the anhydrous compound is obtained. It is very difficult to avoid a partial decomposition on drying. This circumstance interferes to some extent with the

accuracy of the analysis. The following numbers were obtained with the dried base, which agree with the formula $C_{14}H_{14}N_4$.

	Theory for $C_{14}H_{14}N_4$.		Found.			
			I.	II.	III.	IV.
C....	168	70·6	70·07	69·71	69·71	—
H....	14	5·9	6·29	6·53	6·70	—
N....	56	23·5	—	—	—	22·31
	238	100·0				

This compound, the investigation of which is being continued, yields with acids two series of salts; the neutral salts are stable and of a violet colour, the acid salts decompose on addition of water; they are grass-green.

Although the analytical data for this substance (the preparation of which is difficult and expensive) are hardly as satisfactory as could be desired, its great analogy with the one previously described, and its mode of formation, point to but one formula for its constitution—



I hardly venture to draw conclusions from a few experiments with a class of bodies which have as yet no analogues amongst well-known substances. There is one thing, however, which appears to be a rule in reactions of this kind. If a base or a mixture of bases containing amido- and methyl-groups be subjected to the influence of dehydrogenising agents, both NH_2 and CH_3-groups are attacked simultaneously and uniformly, both losing the same amount of hydrogen. The atomicities thus liberated are linked together and form chromophoric groups, which impart the nature of a dye to the new compound. The use of nitroso-compounds is a simplification of this process, and a novel method of avoiding the use of an organic oxidising agent. It is a most convenient means of research, which will furnish us, I have no doubt, with a large number of new and interesting bodies.

I have included in my research the action of other nitroso-compounds on the substances previously enumerated, but I shall refrain for the present from investigating their action upon phenols which do not contain the CH_3-group, as I believe that experiments on that subject are being carried on in another laboratory.

XLIII.—*On a Method of Precipitating Manganese entirely as Dioxide, and its Application to the Volumetric Determination of Manganese.*

By John Pattinson, F.C.S., Newcastle-on-Tyne.

Many methods of determining manganese volumetrically have been from time to time suggested by various chemists, but none have, as yet, come into general use, although a ready means of quantitatively determining this metal has been much needed in metallurgical laboratories since alloys of manganese have been so largely employed in the manufacture of steel. For the most part these proposed methods have been based on obtaining the manganese in a known and definite state of oxidation, and, after determining the amount of oxygen in the oxide over and above that which exists as monoxide, to calculate therefrom the amount of manganese. Some of these methods have failed because, in practice, it has been found that they are more troublesome than the gravimetric methods they were intended to supersede; but, I have no doubt, most have failed from the difficulty or impossibility of obtaining the whole of the manganese in the necessary definite and uniform state of oxidation.

M. Pereño has described (*Ann. Chim. Phys.* [5], **11**, 571—574) a method of determining manganese in manganiferous iron ores, in which a weighed quantity of the ore is calcined for the purpose of converting the whole of the manganese into manganoso-manganic oxide (Mn_3O_4), and afterwards determining, by Bunsen's method, the amount of chlorine produced on heating the oxide with hydrochloric acid. This method, in my hands, with the utmost care, has yielded very irregular results, making an ore containing 20 per cent. of manganese to indicate amounts varying from 17 to 25 per cent. of manganese. These variations are due to the irregular oxidation of the ore during the calcination, and I consider the method altogether untrustworthy on this account.

Lenssen's method—adding the solution of manganese mixed with a ferric salt to a boiling alkaline solution of potassium ferricyanide, and afterwards determining the amount of dioxide formed—as described in the latter editions of Fresenius' "Quantitative Analysis," has also given me irregular results, in one instance only 81 per cent. of the manganese being precipitated as dioxide.

Messrs. Wright and Luff have recently shown ("Report on Researches on some points in Chemical Dynamics," *Journal of the Chemical Society*, vol. **33**, page 513) that certain methods usually prescribe for producing hydrated manganese dioxide do not yield this

oxide alone, but a mixture of dioxide with lower oxides of manganese; thus, the precipitate formed by adding caustic soda to a solution of pure manganous chloride and afterwards digesting for 48 hours in excess of bromine, was found by them to consist of oxides in which 82·46 per cent. of the manganese existed as dioxide, and 17·54 per cent. as monoxide, or oxides equal to these, and that the precipitate formed by boiling potassium permanganate solution with dilute nitric acid was, similarly, found to consist of oxides in which 85·64 per cent. of the manganese existed as dioxide and 14·36 per cent. as monoxide.

I have carefully tried other methods usually recommended for obtaining manganese dioxide from a solution of monoxide. On adding excess of solution of calcium hypochlorite (bleaching powder) to a solution of pure manganous chloride and heating, the whole of the manganese is precipitated, not all, however, as dioxide, but as a mixture of this oxide with lower oxides. In one instance the precipitate thus formed contained 97·5 per cent. of its manganese as dioxide, and in another 98·5 per cent.

Kämmerer and Waage's methods of precipitating manganese from an acetic acid solution by means of bromine, chlorine, and calcium or sodium hypochlorite, were also frequently tried, but it was always found that not more than from 95 to 99 per cent. of the manganese could be obtained as dioxide.

Numerous modifications of these and other methods were tried, but all failed to precipitate the manganese wholly in the desired state of oxidation.

The precipitates of hydrated manganese oxides obtained by these methods were tested for the amounts of dioxide they contained by adding them to a carefully measured quantity of solution of ferrous sulphate containing excess of sulphuric acid, and afterwards determining the amount of unoxidised ferrous sulphate remaining by a standard solution of bichromate of potash.

The above-named experiments were made with weighed portions of pure manganoso-manganic oxide (Mn_3O_4) carefully prepared from very pure crystals of manganous sulphate in the following manner. The manganese in a solution of the manganous sulphate was precipitated by ammonium sulphide, the precipitate washed to free it from a slight trace of lime it contained, redissolved in hydrochloric acid and precipitated as manganous carbonate by ammonium carbonate. After washing the precipitate until it was free from chlorides, it was ignited at a high temperature in a muffle furnace until it ceased to change in weight. The purity of the Mn_3O_4 was carefully tested by precipitation with bromine, and also by determining the amount of excess of oxygen over MnO it contained.

After numerous experiments it was at last found that the whole of the manganese in a manganous chloride solution could invariably be precipitated in the condition of dioxide, *if a certain amount of ferric chloride be also present in the solution*, when a sufficient excess of solution of calcium hypochlorite or bromine-water is added, and, after heating the solution to from 140° to 160° F. (60° to 70° C.) excess of calcium carbonate is then added, and the mixture well stirred.

When the ferric salt is absent and the other conditions are observed, that is, when excess of solution of calcium hypochlorite or bromine water is added to a solution of pure manganous chloride, then, after heating to about 150° F., adding excess of calcium carbonate and stirring, the precipitate invariably contains a certain proportion of lower manganese oxides, the amount of manganese precipitated as dioxide varying from 98·20 to 99·27 per cent. of the amount of manganese present in the solution.

It is difficult to understand why ferric oxide should have this effect on the condition of the manganese precipitate under the circumstances described. Probably in the absence of iron a portion of the manganese is precipitated in a lower state of oxidation as manganite of manganese, but when ferric oxide is present, it takes the place of the basic manganese.

Heat is also essential in order to obtain all the manganese as dioxide, for if the precipitation is made by calcium hypochlorite and calcium carbonate in the presence of much ferric chloride *in the cold*, the precipitate then contains only from 98 to 99 per cent. of its manganese as dioxide.

I have also experimented carefully to ascertain the amount of ferric chloride necessary to cause the whole of the manganese to be precipitated in the desired condition of dioxide, and I find that if there is at least half as much iron as manganese present in the solution, it is sufficient. In practice, however, I prefer to have about equal quantities of each metal in solution. A large excess of iron is no disadvantage.

When equal quantities of manganese and iron are present, and the other conditions fulfilled as described, I have found, by numerous experiments, that the whole of the manganese is precipitated as dioxide, the results I have obtained having almost invariably indicated from 99·95 to 100·12 per cent. of the manganese precipitated in this form when operating on portions of from 3 to 6 grains of pure manganoso-manganic oxide.

In order to ascertain if alumina had the same effect as iron on the character of the precipitate, a solution of alum was added to a known weight of manganese, and treated in the manner above described. Only 98·6 per cent. of the manganese was precipitated as dioxide.

Barium chloride was also tried in the same way, but only 99·18 per cent. of the manganese was precipitated as dioxide in this case. Neither aluminium nor barium salts have therefore the same effect as ferric chloride.

I will now describe the manner in which I use the above mentioned reaction for the quantitative determination of manganese, and this will be done best by giving the details of my method in its application to the testing of manganiferous iron ores, spiegeleisen, ferromanganese, steel, &c., for manganese.

The following are the special solutions and other special reagents required in the process. These are all in ordinary use in metallurgical laboratories, or can be readily obtained. They are :—

1st. *Solution of calcium hypochlorite* (*bleaching powder*).—The solution I use is made by diffusing in 10,000 grains of water 150 grains of ordinary bleaching powder or chloride of lime, containing about 35 per cent. of available chlorine. The clear solution is separated from the insoluble portion by decantation or filtration and bottled for use.

2nd. *Calcium carbonate.*—It is desirable that this should be of a light granular pulverulent character, so that it can be readily diffused through the solution and does not form clots which fall at once to the bottom of the beaker in which the precipitation takes place. This kind of carbonate of lime can often be had from the dealers in reagents; but it may be formed when solutions of calcium chloride and sodium carbonate are added together at a temperature of about 180° F., keeping the calcium chloride slightly in excess, and washing the precipitate well and drying.

3rd. *Solution of ferrous sulphate in excess of sulphuric acid.*—The solution I use contains about 10 grains of iron in 1,000 grains of solution, and is made by dissolving crystals of ferrous sulphate in a mixture of one part of monohydrated sulphuric acid, and three parts of water. 530 grains of crystals in 10,000 grains of the dilute acid give a solution containing about 10 grains of iron in each 1,000 grains.

4th. *Standard solution of potassium dichromate.*—The solution I use is made so that 1,000 grains of it are equal to 10 grains of iron, and is the solution I use in the determination of iron in iron ores, &c. It should be carefully standardised.

Manganiferous Iron Ores.

These ores usually contain from 15 to 25 per cent. of manganese, and at least 20 per cent. of iron; they therefore usually contain an amount of iron sufficient for the dioxide precipitation. 10 grains of the ore, dried at 212° F., are placed in a beaker of about 20 oz.

capacity and dissolved, by the aid of heat, in about 100 fluid grains of hydrochloric acid of about 1·180 sp. gr. When completely dissolved, the cover and sides of the beaker are rinsed by a jet of cold water, and then calcium carbonate is added until the solution becomes of a slightly reddish colour, showing that the free acid is neutralised. Six or seven drops of hydrochloric acid are now added in order to slightly acidify the solution, as it is found that the precipitate falls in the best condition for being filtered and washed when this is done. About 1,000 grains of the solution of bleaching powder are now added, and then boiling water is run in until the solution is heated to about 140 to 160° F. The point when the right temperature has been reached may be ascertained with sufficient accuracy by applying the hand. About 25 grains of calcium carbonate (which, for convenience, may be measured) are now added, and the solution well stirred until the evolution of carbonic acid ceases. The dark-brown precipitate of oxides of manganese and iron settles readily, generally leaving a colourless supernatant liquid, but if the bleaching powder has been much in excess the supernatant liquid has sometimes a pink colour, owing to the formation of permanganic acid. Should this be the case a few drops of alcohol are added until the pink colour is destroyed. If sufficient bleaching powder has been added, the solution smells of chlorine, or it may be tested for excess by a strip of iodised starch paper.

Instead of the solution of bleaching powder, about 500 grains of saturated bromine-water may be used. In this case it is unnecessary to add any acid after the neutralisation of the solution by calcium carbonate, as sufficient acid is formed in the reaction. Care must be taken that sufficient calcium carbonate is present to neutralise all free acid at the end of the precipitation.

The precipitate is now collected on a double filter of sufficient capacity, and washed with cold or warm water until the washings show no trace of chlorine or bromine when carefully tested by iodised starch paper. The washing is readily accomplished and rarely takes longer than a quarter of an hour.

1,000 grains of the acidified ferrous sulphate solution are now carefully measured from a pipette into the beaker in which the precipitation has been made, and which usually contains a small quantity of adhering dioxide, and the filter with its contents is removed from the funnel and placed in the iron solution. The precipitate very readily dissolves even in the cold solution, the manganese dioxide converting its equivalent of ferrous sulphate into ferric sulphate. A sufficient amount of cold water is now added, and the amount of ferrous sulphate still remaining in the solution is ascertained by adding from a burette the standard solution of potassium dichromate just as in the testing of an iron ore.

The exact amount of ferrous sulphate existing in the 1,000 grains of ferrous sulphate solution at first is determined by measuring another 1,000 grains from the pipette, and, after adding a filter to it of the size used in collecting and washing the precipitate, titrating it with the potassium dichromate solution. Sometimes filtering paper has a slightly reducing action, and the influence of this is thus counteracted. It is, however, quite easy to obtain filtering paper that has no reducing action on the solution; but it is safer to standardise after adding a filter to the solution as I have directed.

Supposing the 1,000 grains of ferrous sulphate solution used in standardising has required 101·1° of dichromate solution (I use a burette graduated to hold 150° of 10 grains each, or 1500 grains) and the 1,000 grains to which the manganese precipitate obtained in testing an ore has been added has required 57·0° of the dichromate solution, the percentage of manganese in the ore is calculated as follows: 101·1 —57·0 = 44·1° of dichromate solution, which are equal to 4·41 grains of iron, the amount of iron converted from ferrous to ferric sulphate by the manganese dioxide yielded by 10 grains of the ore. On multiplying the amount of iron thus peroxidised by 0·491 the total amount of manganese contained in the ore is ascertained. In this case 4·41 × 0·491 = 2·165 grains of manganese in the 10 grains of ore, equal to 21·65 per cent.

Should the ore to be tested be a rich manganese ore containing less iron than one half of the manganese it contains, it will then be necessary to add a sufficient amount of ferric chloride free from manganese. As before mentioned, I prefer having about equal parts of manganese and iron in solution when the precipitation is made. The ferric chloride I use for this purpose, and which was used in the above-mentioned experiments with pure Mn_3O_4, is prepared by precipitating the ferric oxide in a ferric salt once or twice with calcium carbonate, and washing so as to get rid of the small amount of manganese which even the purest iron wire contains. The ferric oxide is then dissolved in hydrochloric acid and made up to a known bulk.

For the amounts of bleaching powder solution and other reagents mentioned above, it will be necessary to operate upon such a quantity of the sample as will not contain much more than about 2·5 grains of manganese. If larger quantities are taken, then the amounts of the reagents must also be proportionately increased. But it is unnecessary to operate upon a larger quantity than I have indicated, seeing that with this quantity there is no difficulty in obtaining results which agree within a tenth of a per cent.; moreover the bulk of the precipitate from such a quantity, and the amounts of the solutions required, are convenient to work with.

If it is preferred, a larger quantity of the ore—say 50 or 100 grains

—may be dissolved, and the solution made up to a known bulk in a measuring flask, from which measured portions may be taken.

It is necessary to standardise the ferrous sulphate solutions about once a day, as it becomes slowly oxidised on exposure to air.

Spiegeleisen.

This alloy usually contains from 10 to 25 per cent. of manganese and, of course, a sufficient amount of iron for the dioxide precipitation. 10 grains are taken for analysis. This amount is dissolved in about 120 grains of hydrochloric acid with the aid of heat. About 50 grains of nitric acid are then added for the purpose of converting the ferrous into ferric chloride. After washing the cover and sides of the beaker with cold water, the excess of acid is neutralised by the addition of calcium carbonate until the solution has a reddish colour. 1,000 grains of the bleaching powder solution or about 500 grains of bromine-water are added, without previous addition of hydrochloric acid as in the case of ores. Hot water is then added to heat the solution to 140—160° F., and then about 25 grains of calcium carbonate, and the solution well stirred. The rest of the process is conducted as before described.

Ferro-Manganese.

For the quantitative analysis of this alloy an amount which contains from two to four grains of manganese may be taken. The solution is made as in the case of spiegeleisen. If the alloy contains less iron than manganese, ferric chloride is added so as to make the amounts of the two metals in the solution about equal.* The amount of bleaching powder solution to be added must depend upon the amount of manganese in solution, taking care to add about 400 grains of bleaching powder solution of the strength above-named for every grain of manganese present.

As in the case of ores, instead of weighing off separately the amounts required for each test, a larger quantity may be dissolved

* Since the above was written I have ascertained that F. Kessler recommends the use of zinc chloride for the purpose of preventing the formation of lower oxides than dioxide when manganese is precipitated from its solutions (*Zeitschr. Anal. Chem.*, 1879, 1—14). The method by which he proposes to utilise this reaction for the volumetric analysis of manganese, is, in my opinion, too troublesome and complicated for ordinary use; but I have tried the use of zinc chloride, instead of ferric chloride, as applied to my method of precipitation and analysis, and find it answers equally well, and that it is sufficient to have about as much zinc as manganese present in solution. In cases, therefore, where a sufficient amount of iron is not already present, an addition of zinc chloride may be substituted for the ferric chloride above recommended.

and peroxidised, and, after making up the solution to a known bulk in a measuring flask, the necessary quantities for the test measured out.

Steel.

50 grains of steel are dissolved, by the aid of heat, in about 350 grains of hydrochloric acid of about 1·180 sp. gr. The ferrous chloride thus formed is then converted into ferric chloride by the addition of about 90 grains of nitric acid of about 1·400 sp. gr. The solution is made in a beaker of about 35 oz. capacity. Calcium carbonate is then added until the solution is slightly red. 135 grains of calcium carbonate are now weighed or measured, and about one-half of this added to the solution. After the effervescence caused by the escape of carbonic acid has ceased about 400 grains of the bleaching powder solution are added, and then hot water to heat to about 150° F., and then the remainder of the calcium carbonate. If all the calcium carbonate is added at once the effervescence is so great that the substance is likely to froth over the edges of the vessel; and if the bleaching powder solution is added before any calcium carbonate has been added, the chlorine is likely to be expelled by the evolution of the carbonic acid. The calcium carbonate is, therefore, added at twice, and the bleaching-powder solution between the two additions. The precipitate is then thrown on a sufficiently large filter, and washed until free from any trace of chlorine. Although the precipitate is bulky it is very readily washed.

About 200 grains of the ferrous sulphate solution are standardised and the same quantity used for decomposing the manganese dioxide in the case of steels; but it is sometimes found necessary to add a little additional sulphuric acid, in order to dissolve the ferric oxide precipitate and the excess of calcium carbonate it may contain.

Manganese-Slags, &c.

These are treated similarly to the above, using for the analysis such a quantity as will not contain more than about 2·5 grains of manganese for the above-named amounts of reagents, and taking care to have a sufficient amount of ferric chloride in the solution when the manganese is precipitated.

Should lead, copper, nickel, or cobalt exist in the substance under examination, these must be separated before the manganese is precipitated, as they form higher oxides under the conditions of the precipitation, which oxides, like manganese dioxide, convert ferrous into ferric oxide. Fortunately, in most manganiferous iron ores and in

spiegeleisen, ferro-manganese and steel, none of these metals occur in such quantity as to appreciably affect the correct estimation of the manganese.

Not only is a great saving of time effected by the use of this process instead of the gravimetric process, but in many cases much more accurate results are obtained than by the latter process. This is especially the case in the determination of manganese in manganiferous iron ores, slags, or other substances containing lime and magnesia. When manganese is precipitated by bromine from an ammoniacal solution in the usual way, the precipitate carries down with it small quantities of probably every other base existing in the solution; so that before the exact amount of manganese can be ascertained it is necessary to separate and determine all these substances, and deduct their weight from that of the bromine precipitate. In practice it is usual to separate and determine the amount of baryta the precipitate contains; then to separate the amounts of ferric oxide, alumina, zinc oxide, &c., it contains, and deduct these from the weight of the bromine precipitate; but the lime and magnesia, which the precipitate is also very liable to contain, are not usually separated, and in this way, I think, the amount of manganese in manganiferous iron ores is frequently overstated, sometimes even to the extent of one and a-half per cent. In confirmation of this view the following experiment may be cited. A mixture of 7 grains of pure manganoso-manganic oxide, (Mn_3O_4), 4 grains of calcium carbonate, and 4 grains of magnesium carbonate, was dissolved in hydrochloric acid, and precipitated in the usual way with bromine in ammoniacal solution. The precipitate, after careful washing, drying, and igniting, so as to convert the manganese again into Mn_3O_4, weighed 7·45 grains instead of 7 grains. Had 20 grains of an ore containing these proportions of manganese, lime and magnesia been thus treated, the analysis would have indicated 1·62 per cent. more manganese than the ore actually contained. The precipitate weighing 7·45 grains was afterwards dissolved in hydrochloric acid, and, after precipitating the manganese by ammonium sulphide, amounts of lime and magnesia nearly corresponding with the amount of excess were obtained from the filtrate by the usual processes of analysis. On the other hand, an artificial mixture made to imitate the composition of a natural manganiferous iron ore, and containing, besides 21·5 per cent. of manganese, various quantities of calcium and magnesium carbonate, &c., when tested by the volumetric method I have described, was found by two tests to contain 21·46 and 21·51 per cent. of manganese respectively. The method is therefore much more exact than the usual gravimetric method when testing manganiferous iron ores, slags, &c.

In testing spiegeleisen and ferro-manganese, which do not contain

lime or magnesia, the results of the direct gravimetric method agree very well with those given by the new volumetric method, if, in the gravimetric method, care has been taken to heat the bromine precipitate to a long-continued high red heat, and to separate the iron it usually contains, the differences between the results of the two methods being seldom more than about one-tenth of a per cent. The following are a few of the results I have obtained by both methods of analysis:—

	By usual gravimetric analysis.	By new volumetric analysis.
1	19·81 per cent.	19·89 per cent.
	„ „	19·84 „
2	22·41 „	22·39 „
	22·46 „	22·41 „
3	28·80 „	28·92 „
	28·76 „	28·92 „
4	55·51 „	55·58 „
	55·66 „	55·58 „
5	69·34 „	69·34 „
	69·34 „	69·34 „
6	74·81 „	74·93 „
	74·95 „	74·93 „

The indirect method of determining manganese in spiegeleisen—which consists in determining the iron, assuming the substance contains 5 or 6 per cent. of carbon, silicon, &c., and that the remainder is manganese—is altogether an untrustworthy one. I have known cases where the amount of manganese would have been overstated by more than 2 per cent. if this method of analysis had been adopted.

The new method also answers very well for the determination of manganese in steels. Two portions of 50 grains of pure iron, to which known weights of manganese were added, indicated 0·304 and 0·640 per cent. of manganese instead of 0·302 and 0·604 per cent. respectively. A steel which, by careful gravimetric analysis, was found to contain 0·912 per cent. of manganese, indicated 0·92 per cent. by the new volumetric method.

I have tested very large numbers of samples of manganiferous iron ore, spiegeleisen, and ferro-manganese, by the method I have described in this paper, and have found that the results of the duplicate tests have been almost invariably alike, there being only occasionally a difference of 0·1° or 0·2° in the reading of the burette, equal to 0·05 or 0·10 per cent. of manganese in the sample. In fact, it is now possible to determine manganese volumetrically by this method, as exactly, and almost as speedily, as it is possible to determine iron volumetrically by Penny's well-known bichromate of potash method.

XLIV.—*On the Determination of Nitric Acid as Nitric Oxide by means of its Action on Mercury.*

By Robert Warington.

The determination of nitrogen in the form of nitric oxide gas is, theoretically, one of the most delicate in the whole range of quantitative analysis; firstly, because the measurement of a gas is by far the most exact method of determining the quantity of very small portions of matter; and secondly, because nitrogen in the form of nitric oxide gas occupies twice its own volume. This mode of determination also has the advantage, in common with other reducing methods, of being equally applicable to nitrates and nitrites; while methods based on oxidation, as the determination with indigo, and the measurement of the hydrogen evolved during the solution of aluminium, give unequal values with these two forms of nitrogen.

Two analytical methods are now in use in which nitric acid is estimated in the form of nitric oxide. The first was originated by W. Crum, and has since been improved by Frankland; in this method the conversion of nitric acid into nitric oxide is brought about by the action of the nitric acid upon mercury. The second method is due to Schlœsing; he obtains the nitric oxide by pouring the nitrate to be examined into a boiling solution of ferrous chloride and hydrochloric acid. The first of these methods has been largely employed by Frankland in the execution of water analysis, and has since been adopted for the same purpose by many other chemists. During the last two years the method has been made use of to a considerable extent at Rothamsted; the experience gained in this laboratory will form the subject of the present communication.

In the method described by Crum in 1847 (*Phil. Mag.* [3], **30**, 426), a glass jar, 8 inches long and $1\frac{1}{4}$ inch in diameter, is filled with mercury, and inverted in a mercurial trough. The nitrate to be examined is then passed up in a solid form; 50 grains of water, and 125 grains of oil of vitriol are introduced in a similar manner, and the whole allowed to stand for two hours with occasional agitation. The gas produced is then measured. As a final precaution, a solution of ferrous sulphate is next passed up, and any gas remaining unabsorbed is deducted from the volume first obtained. Crum found that 3 grains of cotton wool might be dissolved in the sulphuric acid, when experimenting with 6 grains of nitre, without injuriously affecting the result. He succeeded in making a good analysis of gun-cotton.

As far as I am aware, Finkener (Rose, *Handb. anal. Chemie*, 6th ed.,

1871, 826) is the only chemist who has published his experience of Crum's method. He states that with small quantities of nitre (0·4 gram) the action is not complete in two hours, but should be allowed to continue for several days.

Frankland and Armstrong (*Chem. Soc. J.*, 1868, 101) have effected a great improvement in Crum's method by conducting the reaction with mercury in a much smaller tube, furnished with a cap and stop-cock at its upper end, through which the solution of nitrate and the sulphuric acid can be introduced. The tube when charged is closed with the thumb, and strongly agitated. The mercury being separated by agitation into small globules, is energetically attacked by the nitric acid, and the reaction is completed in a very few minutes. The gas is then transferred to a gas analysis apparatus, and accurately measured. The authors state that accurate results can be obtained only when the nitrate operated upon is free from chlorides.

W. Thorp (Sutton's *Volumetric Analysis*, 3rd ed., 1876, 316) gives minute directions for the application of Frankland's method to water analysis. He recommends that the relative volumes of the oil of vitriol and the nitrate solution should be about 3 : 2, and the total volume of liquid in the shaking tube about 6 c.c. He directs that gas evolved before shaking has commenced should be expelled from the tube, and not reckoned in the analysis.

In the experiments to be now described Thorp's directions have in the main been carefully followed. A graduated shaking tube was employed, which allowed of the nitrate solution and oil of vitriol being always brought to the same volume. The nitrate solution and rinsings were uniformly 2 c.c., which were increased by the addition of oil of vitriol to 5 c.c. The oil of vitriol employed gave no gas when shaken, as a blank experiment, with distilled water. Some kinds of oil of vitriol give off a small quantity of permanent gas when mixed with water, though containing no nitric acid; such oil of vitriol may be purified by pouring it into water, and then concentrating the diluted acid. Any gas produced before shaking was not expelled, but included in the result, for reasons which will presently appear. In the presence of some kinds of organic matter a very permanent froth was at times produced in the shaking tube, which gave a good deal of trouble when the gas had to be transferred to the measuring apparatus. It was found that the introduction of a drop or two of hot water through the stop-cock frequently destroyed this froth; warming the liquid in the tube, by inclining it while standing in the mercurial trough, so that the upper portion was brought over a small flame, was also effective. The nitric oxide was finally measured in Frankland's latest modification of Regnault's apparatus.

1. *The Influence of Chlorides.*

Following Frankland's direction chlorine was removed in all the earlier experiments by employing a small excess of sulphate of silver. The chloride of silver, when precipitated from solutions containing organic matter, was often troublesome both to filter and wash, a little of the precipitate generally coming through towards the end of the operation. Having obtained some unsatisfactory results, I was led to try if the presence of chloride of silver had any prejudicial effect. A standard nitre solution was prepared from nitrate of potassium, previously fused at a low temperature; portions of 10 c.c. of this solution were evaporated in small beakers with varying proportions of chloride of sodium, with and without the addition of sulphate of silver, the resulting chloride of silver remaining in the beaker. The residues obtained were treated with sulphuric acid in the shaking tube, and yielded the following quantities of nitrogen in the form of nitric oxide.

TABLE I.

No.	Nitrogen taken as potassium nitrate.	Chlorine taken as sodium chloride.	Silver taken as silver sulphate.	Nitrogen obtained as nitric oxide.
	gram.	gram.		gram.
1	·001385	—	—	·001348
2	,,	·000279	—	·001361
3	,,	,,	a slight excess.	·001340
4	,,		,,	·001361
5	,,	·000837	—	·001359
6	,,	,,	a slight excess.	·001349
7	,,	·003650	—	·001360
8	,,	·007300	less than excess.	·001337

The nitrogen obtained is seen to be in all cases a little below the nitrogen taken; this will be found universally the case in the experiments described in this paper; the amount found is not, however, injuriously affected by the presence of a chloride. The differences are very small; but on the whole we should conclude from these figures that the presence of a soluble chloride somewhat raises the result, and thus brings it rather nearer to the nitrogen taken. It will be seen that the maximum amount of chlorine used was rather more than twice the chemical equivalent of the nitrogen present.

To carry the investigation a little further a set of similar experiments was next made with a solution of nitrite of potassium. The amount of real nitrite in the solution was ascertained with a standard solution of potassium permanganate; the total nitrogen was found by shaking with mercury and sulphuric acid, and measuring the nitric

oxide evolved. From these two experiments it appeared that 91·95 per cent. of the total nitrogen existed as nitrous acid. The results obtained with this solution were as follows:—

TABLE II.

No.	Nitrite taken.	Chlorine taken as sodium chloride.	Silver taken as silver sulphate.	Nitrogen obtained as nitric oxide.
		gram.		gram.
1	10 c.c.	—	—	·001548
2	,,	—	a slight excess.	·001533
3	,,	·000279	,,	·001553
4	,,	·003650	—	·001547
5	,,	·007300	—	·001556
6	,,	·030416	—	·001544

Here, as in the experiments with a nitrate, no evil effect appears to follow the presence of a chloride, although chlorine about eight times the equivalent of the nitrogen is in one case present.

The reaction in the presence of a chloride presents an appearance different from that obtained when experimenting with a pure nitrate or nitrite. In the latter case a white turbidity is produced on shaking with mercury, doubtless due to the sulphate of mercury formed in the reaction. When a considerable quantity of chloride is present this turbidity gives place to a copious, dark-grey precipitate, probably mercurous chloride. This precipitate has sometimes a tendency to keep the mercury in the tube in a state of division; and it is possible that with solutions rich both in nitric acid and chlorine, this action of the precipitate may become so considerable as to demand either a dilution of the liquid, or the separation of the chlorine. I have not, however, as yet met with such a case.

I will conclude the evidence respecting the effect of chlorides by giving some determinations of nitric acid in soil, made both with and without the removal of the chlorine. The soils in question were surface soils from an arable field. As 200 or 300 grams of soil were operated on in each case, and the whole of the concentrated extract

TABLE III.

No.	Nitrogen as nitric acid per million of soil, chlorine removed.	Nitrogen as nitric acid per million of soil, chlorine not removed.
1	8·35	8·53
2	5·82	5·83
3	4·94	5·01
4	3·24	4·78
5	1·10	1·07

employed in one experiment, the quantity of chlorine present must have been very considerable.

The tendency on the whole is to slightly higher results where chlorides are present than in their absence; we shall have evidence in the next section that the higher results obtained in the presence of chlorides are probably the more correct.

We may surely conclude from the evidence now adduced that chlorides, except, perhaps, in very extreme cases, are no hindrance to the accurate determination of nitric and nitrous acid by the method under consideration.

2. *Influence of Organic Matter.*

The first experiments I have to quote under this head were made in the Laboratory at South Kensington, by Dr. Frankland's kind permission, during the spring of 1876. Chlorides and ammonium salts were added to the standard nitre solution, as well as various kinds of organic matter, the chlorine being in all cases afterwards removed with sulphate of silver. The object in view was to test the process as applied to water analysis under various trying conditions; for this purpose a rather large excess of silver was usually employed, and the solution then evaporated to dryness, so as to afford every facility for possible change. The amounts of chloride of sodium and organic matter, added to the nitre solution, were unfortunately not determined by weight; the organic matter would probably in every case equal or exceed the quantity of nitre taken.

The 10 c.c. of nitre solution employed in every experiment, contained by calculation ·005056 gram of nitrogen. The results were as follows:—

TABLE IV.

No.	Nitrogen taken, as nitre, ·005056 gram; with the undermentioned substances in addition.	Nitrogen obtained as Nitric oxide.
1	Nitre only	·004954
2	„	·004863
3	„	·004885
4	„	·004934
5	Nitre, with sodium chloride	·004929
6	„ „	·004755
7	„ with ammonium chloride (·005 gram NH_3)	·004803
8	„ sodium chloride, and cane-sugar	·004699
9	„ „	·004526
10	„ ammonium chloride, and dextrin-maltose	·004719
11	„ calcium carbonate 0·1 gram, ammonium chloride = ·0025 gram NH_3, and honey	·004740
12	„ calcium carbonate, ammonium chloride, and isinglass	·004877
13	„ calcium carbonate, ammonium chloride, and a watery extract of pea-flour	·004794

University of Michigan

These experiments were not quite equal in execution to those subsequently made; the total volume of liquid in the shaking tube was for instance variable, and sometimes unnecessarily large.

Experiments 7—10 were made partly to ascertain if the acidification which might possibly occur during evaporation from the reduction of the excess of sulphate of silver, or from the dissociation of ammonium salts, would prejudice the result. In Experiments 11—13 carbonate of calcium was added to prevent this acidification.

The general result appears to be that organic matter, in the quantities actually used, exhibits little power of affecting the result, except in the experiments with cane-sugar.

The reaction in the presence of cane-sugar was remarkable. When the oil of vitriol was added to the nitrate in the shaking tube a lively effervescence took place, and in the case of Experiment 9 about two-thirds of the gas finally obtained was generated without any agitation with the mercury. The first explanation which suggested itself was that the nitrates had become reduced to nitrites during the evaporation with sugar and excess of silver, and that these nitrites were readily decomposed on the addition of sulphuric acid. Further experience of the actual behaviour of nitrites has however shown, that though a little gas is generally yielded by them on the introduction of the oil of vitriol, the amount is always very small in proportion to that obtained on agitation with the mercury.

A more recent series of experiments upon the influence of cane-sugar has thrown some fresh light on the subject. It was desired to determine the quantity of nitrates present in the sap of mangels; to accomplish this it would be necessary in some cases to operate in the presence of 1 gram of cane-sugar. It was found that 1 gram of sugar, dissolved in 3 c.c. of water, might be treated with $4\frac{1}{2}$ c.c. of oil of vitriol in the shaking tube without any evolution of gas, if the acid was not added suddenly, but gradually mixed in successive portions; the resulting liquid was very dark, but not at all viscid. When, however, 10 c.c. of the standard nitre solution were mixed with 1 gram of cane-sugar, the whole evaporated to a syrup, and treated with oil of vitriol in the shaking tube, no gas whatever was obtained on agitation with mercury. A series of test experiments was then made with various proportions of sugar; in some of these experiments a known quantity of chloride of sodium was introduced. The results are shown in the following table:—

TABLE V.

No.	Nitrogen taken, as nitre, ·001388 gram; with the undermentioned substances in addition.	Nitrogen obtained. Actual.	Mean.
1	Nitre only	·001364	·001364
2	„ cane-sugar ·01 gram	·001352	·001271
3	„ „	·001189	
4	„ cane-sugar ·02 gram	·001268	·001177
5	„ „	·001001	
6	„ „	·001252	
7	„ „	·001187	
8	„ cane-sugar ·02 gram, sodium chloride ·02 gram.	·001303	·001259
9	„ „ „ ·04 gram.	·001214	
10	„ cane-sugar ·10 gram	·001183	·001092
11	„ „	·001139	
12	„ „	·000953	
13	„ cane-sugar ·10 gram, sodium chloride ·05 gram.	·001266	·001266.
14	„ cane-sugar ·20 gram	·000768	·000768
15	„ cane-sugar ·20 gram, sodium chloride ·05 gram.	·000812	·000812
16	„ cane-sugar ·50 gram, sodium chloride ·10 gram.	·000381	·000381

A few similar experiments were made with a much stronger solution of nitre; the results were as follows:—

TABLE VI.

No.	Nitrogen taken, as nitre, ·005063 gram; with the undermentioned substances in addition.	Nitrogen obtained. Actual.	Mean.
17	Nitre only	·004993	·004993
18	„ cane-sugar ·02 gram	·004974	·004977
19	„ „	·004980	
20	„ cane-sugar ·10 gram	·004400	·004426
21	„ „	·004452	
22	„ commercial glucose ·10 gram	·004987	·004987
23	„ commercial glucose ·50 gram	·004656	·004656

Three experiments were also made with a solution of nitrite of potassium.

TABLE VII.

No.	Nitrite of potassium solution taken, 10 c.c.; with the undermentioned substances in addition.	Nitrogen obtained.
24	Nitrite only	·001555
25	„ with cane-sugar ·01 gram	·001467
26	„ with cane-sugar ·02 gram	·001339

Looking first at the quantities of nitrogen obtained, we see that

with the weaker solution of nitre (Table V) there is a good deal of variation among the duplicate experiments. This variation will in part be due to changes in the mode of mixing and shaking, made with the hope of obtaining better results; the subject will be again referred to in the next section. In the experiments with the stronger solution of nitre (Table VI) this variation ceases to appear.

The effect of the addition of sugar is clearly to diminish the amount of nitric oxide liberated, whether the nitrogen was present in the form of nitrates or nitrites, the amount of error increasing with the amount of sugar added. In the case of the weaker nitre solution a good result is obtained in one case (Experiment 2) in which the sugar was about equal in weight to the nitre present; but in a duplicate experiment, and with larger proportions of sugar, the results are uniformly too low. With 0·20 gram of sugar (about 20 times the nitre) little more than one-half the nitrogen present is obtained.

In the case of the stronger nitre solution, a quantity of sugar rather more than one-half the weight of the nitre has very little effect. The actual error produced by 0·02 gram of sugar with the stronger nitre solution (a deficiency of 0·000016 gram of nitrogen) is considerably less than that which occurs with the weaker nitre solution (a deficiency of 0·000187 gram); but when the quantity of sugar is increased five times, the actual error is greater with the stronger nitre solution, the deficiency being 0·000567 gram, as compared with 0·000272 gram in the case of the weaker solution. The percentage error is, however, in both cases far smaller with the stronger solution of nitre. The experiments thus show that a small quantity of sugar will occasion a greater error of deficiency in a weak solution of nitre than in a strong solution, and it seems on the whole probable that cane-sugar produces but little effect until its proportion becomes rather considerable in relation to the nitrate present;* the evidence is not however as clear as we should wish.

It would appear from the few experiments made with commercial glucose that this sugar has a considerably less injurious effect than cane-sugar. The commercial glucose used contained doubtless a good deal of water, but this fact is incapable of explaining the difference, as 0·50 gram of glucose is seen to diminish the result much less than 0·10 gram of cane-sugar.†

* With this would agree Crum's successful experiment, in which he employed cotton equal to half the weight of the nitre taken.

† Since writing the above I find that G. Lunge has published (*Deut. Chem. Ges. Ber.*, **11**, 439) an experiment on the influence of glucose in the determination of nitrous acid in oil of vitriol by the Crum-Frankland method. He employed ·009 gram of glucose, and obtained 20·51 c.c. of nitric oxide. Without the glucose the same nitrous oil of vitriol yielded 21·6 c.c. of nitric oxide. He indeed states that without glucose the gas was 20·6 c.c., but this figure is seen by a comparison with

When the quantity of sugar employed did not exceed 0·02 gram, the mixture remained colourless after the careful addition of the oil of vitriol. With 0·10 gram, or more, of cane-sugar, a pale sherry-coloured solution was in most cases finally obtained.

A more important character of the reaction was the evolution of gas before shaking with mercury had commenced. With the weaker solution of nitrate this gas was generally very small in quantity, and never exceeded one-fifth of the volume finally obtained. With the nitrite solution the action before shaking was distinctly more vigorous. With the stronger nitrate solution the action reached its maximum. In Experiment 21, about 5 c.c. of gas, more than half the quantity finally obtained, were generated in about a minute, without any shaking with mercury having taken place. In Experiment 23, as much as 7 c.c. of gas were evolved before shaking, and indeed before the whole of the oil of vitriol could be got into the tube; the solution acquired a pale straw colour. It is noteworthy that in these cases of violent action before shaking, the solution continues to the last perfectly clear, no turbidity due to sulphate of mercury being produced; the action is in fact not between the nitric acid and the mercury, but between the nitric acid and the organic matter. Portions of the stronger nitrate of potassium solution were evaporated on the water-bath, both with cane-sugar and glucose, and the residues examined for nitrite, but none was found; the violent action in the shaking tube does not therefore, as at first imagined, imply the presence of nitrites.

In what manner the presence of cane-sugar is able to diminish the amount of nitric oxide liberated is by no means clear. We arrive, however, at the practical conclusion that gas produced before the agitation with mercury must not be removed, such gas being in some cases nitric oxide. Further, that effervescence before agitation may be evidence of the presence of organic matter, and is then accompanied by low results. We must bear in mind, however, that when the organic matter is in great excess there is no effervescence, no gas whatever being formed. Other kinds of organic matter besides cane-sugar may produce similar results. I have noticed that the concentrated watery extract of soil will in some cases effervesce freely in the shaking tube before agitation has commenced.

One result shown by the experiments on Table V has not yet been noticed; this is the effect of chlorides. Chlorides clearly diminish, though they do not destroy, the prejudicial influence of organic matter. The presence of chlorides, doubtless, increases the energy of

his earlier statements to be a misprint for 21·6. The quantity of glucose he employed was much smaller, and the quantity of gas dealt with much larger than in any of my own experiments.

the attack on the mercury, which is in fact acted on by *aqua regia* in place of nitric acid.

An excellent illustration of the effect of chlorides in improving the results obtained when organic matter is present, has been afforded by the analysis of some of the solutions which have been nitrified at Rothamsted. In a series of experiments not yet communicated to the Society, solutions of chloride of ammonium of known strength have been mixed with small quantities of tartrate and phosphate of potassium, and an excess of carbonate of calcium, and nitrification set up by seeding with a few drops of a solution already nitrified. When ammonia was no longer found in the solution the quantity of nitric acid formed was determined by the indigo method; but to check these results several determinations were also made by Frankland's method, the chlorine being first removed with sulphate of silver. The results obtained on agitation with mercury were, however, hopelessly low, only about half the quantity of nitric acid found by indigo being obtained as gas. The indigo determinations, on the other hand, agreed fairly with the amount of ammonia known to have disappeared. After much vexatious endeavour to reconcile the two methods, the subject was given up as hopeless. When, however, it became known that the removal of chlorides was unnecessary for carrying out Frankland's method, these nitrified solutions were re-analysed, no silver being employed; the results now agreed fairly with those yielded by indigo. The figures obtained for two of the solutions were in parts per million as follows:—

No.	Nitrogen as NH_3 before nitrification.	Nitrogen as nitric acid after nitrification.		
		By indigo.	By Frankland's method.	
			Chlorine removed.	Chlorine not removed.
E	20·8	20·2	12·6	18·5
,,	,,	—	11·6	—
C2	20·5	18·7	9·5	18·8
,,	,,	—	6·4	—

In the case of the solution marked C2, the organic matter present was cane-sugar instead of tartaric acid. This will account for the low result obtained with indigo. Cane-sugar is inimical to the indigo method; tartaric acid is not.

3. *The Amount of Accuracy obtainable.*

A number of test experiments have been recorded in the two pre-

ceding sections, all of them made with pure fused nitre dissolved in calibrated vessels to a known volume, and taken for use with a calibrated pipette. It may be useful to group those results together, in obtaining which neither organic matter nor sulphate of silver was employed, with a view to ascertain the amount of accuracy of which the process is capable.

TABLE VIII.

No.	Material operated on.	Nitrogen present.	Nitrogen found.	Actual deficiency.	Percentage deficiency.
		gram.	gram.	gram.	
1	Nitre only	·001388	·001364	·000024	1·7
2	,,	,,	·001356	·000032	2·3
3	,,	·001385	·001348	·000037	2·7
4	,,	·005063	·004993	·000070	1·4
5	,,	·005056	·004954	·000102	2·0
6	,,	,,	·004934	·000122	2·4
7	,,	,,	·004885	·000171	3·4
8	,,	,,	·004863	·000193	3·8
9	Nitre and sodium chloride	·001385	·001361	·000024	1·7
10	,, ,,	,,	·001360	·000025	1·8
11	,, ,,	,,	·001359	·000026	1·9
12	,, ,,	·005056	·004929	·000127	2·5
13	,, ,,	,,	·004755	·000301	6·0

It is seen at once that all the results show a small deficiency, amounting in the case of the weaker solution of nitre to 0·000028 gram of nitrogen as the mean of six experiments. With the stronger solution of nitre the experiments are not so good, chiefly because all of them save one (No. 4) belong to the first series of experiments, which were somewhat less perfectly carried out.

Besides this small constant deficiency, which is found even in good experiments, there is a tendency under some circumstances to a much greater deficiency, arising from an imperfect action in the shaking tube. When this imperfect action has taken place, and the contents of the shaking tube have been transferred to the laboratory vessel, the surface of the mercury in this vessel will after a time become coated with small bubbles, the quantity of which may increase, though at a diminishing rate, for several days. Two instances of this occurrence will suffice as illustrations.

A standard nitre solution, containing 0·001391 gram of nitrogen, was evaporated with a slight excess of sulphate of silver, and some solution of gypsum, as a test experiment; the residue was treated with sulphuric acid in the shaking tube in the usual manner.

Gas obtained at first	·001082	gram.
Formed in laboratory vessel 1 day ..	·000133	,,
,, ,, 2 days ..	·000124	,,
,, ,, 3 days ..	·000017	,,
Total nitrogen after 6 days	·001356	,,

The next instance I will quote is that of a drainage water from unmanured land, containing by the Indigo method 16·9 parts of nitrogen per million as nitric acid. 100 c.c. treated by Frankland's method, no sulphate of silver being used, gave—

Gas obtained at first	·001421	gram.
Formed in laboratory vessel 1 day....	·000138	,,
,, ,, 1 day....	·000084	,,
,, ,, 4 days ..	·000013	,,
Total nitrogen after 6 days	·001656	,,

This tendency to low results has been a source of much trouble, it being impossible, save in the case of a test experiment, to know whether a result was low except by leaving the acid liquid in the laboratory vessel, and thus preventing the use of the apparatus.

The incomplete reaction in the shaking tube is probably due in part to want of proper manipulation, and it is possible that other chemists may not meet with the same experience. I would suggest that to avoid an imperfect reaction one should be careful not to shake too violently at first, but keep the liquid as far as possible in the upper part of the tube; any liquid introduced between the mercury and the glass must be apt to escape the action. Next, when the action has commenced, endeavour to carry it out to the end with as little check as possible. I have found it a good plan, when fearing low results, to make the liquid in the tube hot with a small flame after the first shaking, and then to shake again; but this plan is attended with danger, as the gas in the tube is cooling rapidly during the second shaking, and there is consequently some risk of air entering from without.

The tendency to an incomplete reaction in the shaking tube will naturally be greater with a weak than with a strong solution of nitrate. This is doubtless a partial cause of the irregularities among the experiments with a weak nitrate solution recorded in Table V. This action, however, by no means explains the low results uniformly given in the presence of sugar, for several of the solutions arising from these experiments, as Nos. 11, 16, and 23, were purposely left in the laboratory vessel a whole day without yielding any more gas, or at most a trace only. The effect of heat was also tried on some of the solutions,

but without any notable result. The presence of chlorides will diminish the tendency to low results.

We may venture to conclude from these trials of the method of Crum and Frankland—

1. That in the absence of organic matter, and with proper manipulation in the shaking tube, the method is one of great accuracy, and capable of determining extremely small quantities of nitrates or nitrites.

2. That the natural error of the method is a small one of deficiency. An imperfect reaction in the shaking tube may, however, take place, arising from faulty manipulation, or other causes, through which low results may be obtained. In such cases the missing gas will be slowly evolved in the laboratory vessel.

3. That the presence of chlorides, at least in moderate quantity, is no hindrance, as was supposed, to the success of the method.

4. That quantities of organic matter small in relation to the nitrates present have little or no effect on the result, but that larger proportions may cause a very considerable deficiency, this being especially proved in the case of cane-sugar. The presence of chlorides tends to reduce the error introduced by the presence of organic bodies, but fails to remove it entirely.

XLV.—*The Alkaloïds of the Aconites.* Part IV. *The Alkaloïds of Japanese Aconite Roots.*

By C. R. Alder Wright and A. P. Luff (Appendix by C. R. Alder Wright and A. E. Menke).

§ 1. *Isolation of Crystallisable Alkaloïd.*

During the past two or three years several importations of aconite roots have been made from Japan. Whether these consist of one single species or of several mixed together does not seem to be certain, nor is the nature of the predominant species clear. According to the observations of Mr. E. M. Holmes, the roots met with commercially appear to be wholly or almost entirely of one kind, and that different in certain respects from German *A. Napellus* roots. That the roots hitherto imported are actually uniform in quality and different from

both *A. Napellus* and *A. Ferox* is rendered probable by the results detailed below; but how far this may be due to climatic influences, and how far it indicates difference of species, is at present not very clear.

The observations of most manufacturers and pharmacists who have had occasion to examine cursorily or in detail these Japanese roots, point either to their being richer in active ingredients than the *A. Napellus* and *A. Ferox* roots ordinarily met with in commerce, or to their containing a more active alkaloïd. Not only is the dust produced in grinding and pulverising much more irritating than that of ordinary aconite roots, but the effects produced on the operator whilst preparing liniments, &c., from the Japanese root, and the irritating action of the liniment on the skin, are, according to Gerrard, far greater than when ordinary aconite roots are employed, so that it is not safe to substitute Japanese roots for the ordinary kinds in the preparation of pharmaceutical tinctures, &c.

A preliminary examination of these roots was made some two years ago by Dr. Paul and Mr. Kingzett (*Pharm. J. Trans.*, Sept. 1, 1877, 172; *Yearbook of Pharmacy*, 1877, 469), who obtained from nearly 4 kilos. of roots nearly 7·2 grams of alkaloïds soluble in ether, partly crystallised, partly varnish-like. This yield, = about 0·18 per cent., is considerably superior to that obtained by one of us from a large batch (2 cwts.) of *A. Napellus* roots, viz., about 0·07 per cent. of alkaloïds soluble in ether (Part I, this Journal, 1877 [1], 143); whence it would seem probable that the greater potency of the Japanese roots is due rather to its containing more of the active ingredient than to this latter being intrinsically more energetic physiologically. The small quantity of crystallised substance obtained in a pure condition by Paul and Kingzett prevented their studying the properties of the alkaloïd and its derivatives as thoroughly as might be desired. They describe it as a well crystallised base, infusible at 100° (its melting point was not determined), giving the following numbers on analysis: carbon, 62·926; hydrogen, 7·900 and 7·726; nitrogen (by volume) 2·567; and not forming any crystallised salts, although many and varied attempts to prepare them were made. The molecular weight was not controlled by the formation of a gold salt, &c. (probably through insufficiency of material); hence, regard being had to the probable imperfect accuracy of nitrogen determinations by volume, it is evident that the formula deduced by them from the above numbers (viz., $C_{29}H_{43}NO_9$, requiring carbon, 63·38; hydrogen, 7·83; nitrogen, 2·55), can only be regarded as an approximation to the truth, especially as this formula requires not only more hydrogen than that found in one of the two determinations, but slightly more than that given by the mean of these two. As pointed out by one of us during the discussion

on the paper, the numbers obtained and most of the properties of the crystallised alkaloïd are quite compatible with the possibility of this base being simply pseudaconitine, $C_{36}H_{49}NO_{12}$, which requires carbon, 62·88; hydrogen, 7·13; nitrogen, 2·04; numbers almost exactly the same as those deducible from Paul and Kingzett's analysis, after making allowance for the probable excesses of hydrogen and nitrogen found, whilst the difficulty in forming crystallised salts, noticed by Paul and Kingzett, is precisely that noticed with pseudaconitine, the gold salt and nitrate of which are the only salts yet obtained crystallised; the preparation of these crystalline salts, moreover, requires peculiar manipulation, the nature of which was not known at the time of the publication of their results (Part II). On the other hand, the crystallisability of the base obtained by Paul and Kingzett appeared to them to be much higher than that of pseudaconitine, wherefore they were disposed to regard it as a distinct alkaloïd. This view, moreover, is borne out by the fact observed by them, that on boiling their base with dilute sulphuric acid a liquid was obtained capable of reducing Fehling's solution. Now pseudaconine, producible in this way from pseudaconitine, does not reduce Fehling's solution, although aconine, the corresponding saponification-product of aconitine, does do so. It hence appears at least probable that the base examined by Paul and Kingzett was a saponifiable one like aconitine and pseudaconitine, in which case a simple explanation is given of the circumstance noticed by Paul and Kingzett, that the mother-liquor of the base when recrystallised from hot dilute alcohol contained an organic *salt* of an alkaloïd in solution. Doubtless the original alkaloïd became partially saponified by the hot aqueous liquid, just as pseudaconitine does under similar conditions (Part II). Paul and Kingzett, however, considered that the occurrence of a salt in the mother-liquors pointed to the solution by ether of this salt (possibly aconitate) during the extraction of the alkaloïds; a most unlikely thing to happen, considering that the ether was applied in presence of excess of alkaline bicarbonate, which must inevitably have decomposed such a salt, forming the corresponding sodium salt, carbon dioxide, and the free alkaloïd.

Paul and Kingzett having, through various circumstances, relinquished the further investigation of these Japanese aconite roots, and the nature of the contained alkaloïds being thus in an uncertain state, we have, at the request of the Pharmaceutical Conference (to which our thanks are due for several money grants for carrying out the following experiments, as well as those detailed in Parts I, II, and III), made a careful examination of the subject. Our results (obtained with two different batches of roots), as well as some further results (obtained with a third batch by one of us and Mr. A. E. Menke) detailed in an appendix to this paper, indicate that the view held by

Paul and Kingzett that Japanese aconite roots contain an alkaloïd different from both aconitine and pseudaconitine, and peculiar to themselves, is correct. Practically identical analytical numbers were obtained, not only with all three batches of roots, but also with each fraction into which each batch of crystallisable alkaloïd was fractionated, with a view to finding out whether the substance obtained was a mixture of more than one base. These numbers, whilst not far removed from the percentages obtained by Paul and Kingzett, lead to a formula considerably different from that assigned by them, the molecular weight being much higher. The alkaloïd, which thus appears to be the only crystallisable one contained, presents many resemblances to aconitine, and, like that base, splits up into benzoic acid and a derivative closely resembling aconine. This latter saponification-product reduces Fehling's solution, whence it appears probable that the substance extracted by Paul and Kingzett was actually the same as that obtained by us. It is difficult, however, to understand why in that case Paul and Kingzett failed to obtain crystallised salts, as every specimen of base obtained by us readily yielded a well crystallised nitrate hydrochloride and hydrobromide on simply stirring a pulverised crystal in a watch glass with a little dilute acid. Solution to a clear fluid at first took place, and on further stirring, a crystallised magma of the respective salt was formed, just as with aconitine.

The first batch of roots examined by us was obtained from Messrs. Wright, Layman, and Umney: about 14 kilos. of ground root were percolated with alcohol acidulated with tartaric acid, 1 part of acid per 100 of roots being employed: the percolate was evaporated to a small bulk, diluted with water, strained from precipitated resinous matter, shaken with ether whilst still acid to remove remaining resinous matter, and then rendered slightly alkaline with sodium carbonate, and shaken repeatedly with ether, the ethereal solutions being shaken with aqueous tartaric acid, and used over again. After some six treatments with an equal bulk of ether, but little alkaloïd was dissolved out, and this little appeared to be non-crystalline; the alkaline liquors, however, contained (as remarked by Paul and Kingzett, and like the corresponding liquors from *A. Napellus*—Part I) some amount of alkaloïdal matter in solution; this was examined as described below (§ 5), but appeared to contain only non-crystalline basic matter. The crude tartaric acid solution of bases thus obtained was treated with sodium carbonate and fresh ether, and the ethereal solution allowed to evaporate spontaneously: a copious crop of crystals was obtained with a quantity of viscid alkaloïdal matter, readily soluble in alcohol and ether. By filter-pumping and washing the crystals were obtained pretty free from amorphous bases: the filtrates on spontaneous evaporation deposited a few more crystals, too small in quantity for examination; finally there

were obtained about 12 grams of crystallised base and 25 of resinous basic matter from the filtrates, corresponding to about 0·08 per cent. of crystals, and 0·17 per cent. of amorphous bases, = 0·25 per cent. in all, or somewhat more than was obtained by Paul and Kingzett, who obtained a total yield of about 0·18 per cent.

The first crystals deposited were purified by several crystallisations from ether, and were then marked (A): on analysis they yielded numbers close to those required for apo-aconitine, whence we were at first inclined to suppose that the alkaloïd originally present was aconitine, and that it had been partially dehydrated during extraction by the tartaric acid: this view, however, was negatived by the fact that just the same numbers were obtained after converting crystals (A) into hydrobromide, recrystallising the salt, and regenerating the alkaloïd (Specimen B); whilst no change was introduced by repeating the purification by again converting into hydrobromide, crystallising the salt, and regenerating the base (Specimen C). Moreover the mother-liquors of the first crop of crystals of hydrobromide were treated with sodium carbonate and ether, and the base that crystallised from the ether examined (Specimen D). In all four cases numbers were obtained which, though not far from those required for apo-aconitine, were yet sufficiently removed therefrom to indicate a difference, the carbon and especially the hydrogen found being uniformly higher than the values got on examination of pure apo-aconitine (Part III).

The second batch of roots was worked up by Messrs. Hopkin and Williams in the same way as that above described, being percolated with alcohol acidulated with tartaric acid (1 part per 100 of roots). The bases soluble in ether finally obtained were sent to us without purification as a nearly white amorphous powder; on dissolving this in tartaric acid, adding sodium carbonate, and shaking with ether, the whole dissolved: on spontaneous evaporation about 60 per cent. of the rough alkaloïdal mass was obtained as crystals, and 40 as non-crystalline basic matter from the ethereal mother-liquors. The crystals thus obtained after washing with ether were stirred up with warm dilute nitric acid; on standing and adding a little concentrated nitric acid a magma of crystals was formed, which was separated by the pump filter and washed with dilute nitric acid: from these crystals the base was regenerated by soda and ether (Specimen E). The mother-liquors of these crystals were treated with soda and ether, and the crystals that separated examined (Specimen F). Finally, Specimen E was converted into hydrobromide, the salt recrystallised, and the base regenerated by soda and ether (Specimen G).

The numbers obtained with all seven of these specimens are practically identical: each sample was anhydrous when air-dry.

Specimen (A) 0·2770 gram gave 0·6440 CO_2 and 0·1845 H_2O.
0·3555 „ gold salt gave 0·0730 Au.
„ (B) 0·2580 „ gave 0·6010 CO_2 and 0·1745 H_2O.
„ (C) 0·2600 „ „ 0·6045 CO_2 and 0·1735 H_2O.
0·5670 „ burnt with soda lime gave by titration 0·01285 N; by platinum salt, 0·0910 Pt.
0·6780 gram gold salt gave 0·1380 Au.
„ (D) 0·2755 „ gave 0·6425 CO_2 and 0·1850 H_2O.
0·4705 „ gold salt gave 0·0965 Au.
„ (E) 0·2960 „ gave 0·6920 CO_2 and 0·1985 H_2O.
0·5965 „ gold salt gave 0·1230 Au.
„ (F) 0·2775 „ „ 0·6500 CO_2 and 0·1850 H_2O.
0·3360 „ „ 0·7840 CO_2 and 0·2365 H_2O.
0·1940 „ „ 0·0395 Au.
„ (F) 0·5340 „ gold salt gave 0·1095 Au.
„ (G) 0·3035 „ gave 0·7060 CO_2 and 0·2055 H_2O.
0·5235 „ gold salt gave 0·1060 Au.
0·3495 „ burnt with soda lime, gave by titration, 0·00799 N; by platinum salt, 0·056 Pt.

Specimen.	In free base. Carbon.	Hydrogen.	Nitrogen.	In gold salt. Gold.
A	63·41	7·40	—	20·53
B	63·52	7·51	—	—
C	63·41	7·41	2·27 2·27	20·35
D	63·60	7·45	—	20·51
E	63·76	7·45	—	20·62
F	63·88	7·41	—	20·36
	63·63	7·82*	—	20·50
G	63·44	7·52	2·29 2·26	20·24
	63·58	7·50	2·27	20·44

The constancy of the numbers obtained with these different fractions apparently excludes the possibility of their being mixtures of two different bases, and hence renders it improbable that they consisted of two bases, $C_{33}H_{45}NO_{11}$ and $C_{33}H_{43}NO_{10}$, mixed in about equivalent proportions; for the results obtained with aconitine and pseudaconitine indicate that had this been the case the fractionations would have more or less completely separated these constituents. Such a mixture,

* This combustion was made in the old-fashioned way by mixing with oxide of copper; the others were all done by the breech-loading process, the substance to be burnt being introduced in a platinum boat, and the combustion finished in a stream of oxygen.

however, would very closely correspond with the numbers found, inasmuch as it would require as follows:—

	Calculated for $C_{33}H_{45}NO_{11}$ + $C_{33}H_{43}NO_{10} = C_{66}H_{88}N_2O_{21}$.	Found.
Carbon in base	63·67	63·58
Hydrogen „	7·07	7·50
Nitrogen „	2·25	2·27
Gold in gold salt.....	20·39	20·44

Moreover, had the substances examined been mixtures of two bases, $C_{33}H_{45}NO_{11}$ and $C_{33}H_{43}NO_{10}$, related as aconitine and apo-aconitine or as pseudaconitine and apo-pseudaconitine, prolonged heating with concentrated tartaric acid solution should have converted the mixture wholly into $C_{33}H_{43}NO_{10}$, requiring carbon 64·60, hydrogen 7·01, nitrogen 2·28, Au in gold salt 20·57; but as shown below (§ 2) no change whatever in composition was thus produced, no increase in carbon percentage being caused by the treatment: hence, since no simple mono-nitrogenous formula agrees well with the average numbers found, and since the formula, $C_{66}H_{88}N_2O_{21}$, expresses them perfectly, it results that in all probability this formula expresses the true composition of the single base isolated. It is noticeable that a substance of this composition might be supposed to be formed from a base, $C_{33}H_{47}NO_{12}$, by the removal of water as follows:—

$$2C_{33}H_{47}NO_{12} = 3H_2O + C_{66}H_{88}N_2O_{21},$$

and that this hypothetical parent base, $C_{33}H_{47}NO_{12}$, only differs from aconitine, $C_{33}H_{43}NO_{12}$, by H_4. The results detailed below (§ 4) as to the action of benzoic anhydride on the crystallised base isolated as above described, and the nature of its saponification-products (§ 3), viz., benzoic acid, and a base containing H_4 more than apo-aconine, go far to indicate that this view of its formation, if not absolutely correct, is not far from the truth: as stated in the Appendix, however, attempts to isolate the hypothetical parent base, $C_{33}H_{47}NO_{12}$, by treating Japanese roots with alcohol not acidulated by any acid at all, so as to avoid as far as possible dehydrating action, did not lead to this result, only the base, $C_{66}H_{88}N_2O_{21}$, being thus obtained.

In order to avoid circumlocution, it is proposed to refer to the crystallised base actually isolated, $C_{66}H_{88}N_2O_{21}$, as *Japaconitine*, and to its saponification-product (§ 3) as *Japaconine*. Should, however, the existence of the hypothetical parent base, $C_{33}H_{47}NO_{12}$, be hereafter substantiated, and the formation of $C_{66}H_{88}N_2O_{21}$ from it by dehydration as above be proved, it perhaps might be more convenient to term the parent base japaconitine, and the derivative "sesqui-apo-japaconitine,"

when the saponification-product would become "apo-japaconine" (*vide* § 3 and 4 and Appendix, conclusion).

The seven specimens of japaconitine above described melted in capillary tubes at temperatures lying between 184° and 186° corrected in each case; or from 1° to 2° higher than aconitine tested side by side, and sensibly at the same temperature as apo-aconitine. In Part I, by an uncorrected error of the press, 189° is given as the melting point of aconitine, instead of 183—184°.

Japaconitine hydrobromide crystallises, like aconitine hydrobromide, with $2\frac{1}{2}H_2O$ per C_{33} present.

1·0925 gram of air-dry hydrobromide from the first batch of roots (the salt from which specimen B was prepared) lost at 100° 0·0685 gram = 6·27 per cent.

0·8575 gram of the salt from which specimen C was prepared lost 0·0560 = 6·53 per cent.

1·0240 gram of the salt from which specimen G was prepared, lost 0·0620 = 6·05 per cent.

Calculated for $C_{66}H_{88}N_2O_{21}$, 2HBr, $5H_2O$ = 6·02 per cent.

§ 2. *Action of Concentrated Tartaric Acid Solution on Japaconitine.*

It has been shown in Parts II and III, that when aconitine and pseudaconitine are heated for some hours with concentrated tartaric acid solution to 100°, the elements of water are removed, and apo-derivatives formed. Japaconitine (Specimen G) was heated to 100° for eight hours with a large excess of nearly saturated tartaric acid solution; on treatment with soda and ether, a base crystallised precisely resembling japaconitine in all respects, and yielding on combustion precisely the same numbers as the original substance; wherefore no dehydration had taken place.

(I.) 0·2750 gram gave 0·6370 CO_2 and 0·1820 H_2O after conversion into crystallised nitrate, filter-pumping, and regenerating by soda and ether.

(II.) 0·2470 gram gave 0·5735 CO_2 and 0·1645 H_2O.

	Calculated for $C_{66}H_{88}N_2O_{21}$.	Original substance. Specimen G.	I.	II.
Carbon	63·67	63·44	63·17	63·32
Hydrogen	7·07	7·52	7·35	7·40

The melting point was unaltered.

§ 3. *Action of Saponifying Agents on Japaconitine.*

On heating japaconitine with alcoholic potash saponification rapidly takes place, being complete at the end of a few hours; by evaporating

off the alcohol, treating the residue with dilute sulphuric acid and ether, and allowing the ethereal solution to evaporate spontaneously, benzoic acid with a small quantity of resinous feebly acid bye-product is obtained, just as with aconitine (Part III).

0·880 gram from first batch of roots worked up gave of benzoic acid containing a little resinous matter, 0·1730: on titration with decinormal soda this corresponded to 0·1715 $C_7H_6O_2$.

1·9665 gram from second batch of roots gave 0·4410 gram of benzoic acid containing resinous matter; by titration this corresponded to 0·412 $C_7H_6O_2$.

Calculated benzoic acid per 100 parts of japaconitine.	Found. By titration.	By weighing.
19·6	19·5	19·6
—	20·9	22·4

This benzoic acid agreed in all respects with ordinary benzoic acid; it melted at 120·5°, and gave a silver salt of which

0·2120 gram gave 0·1000 Ag = 47·17 per cent.

Calculated for $C_7H_5AgO_2$ = 47·16 per cent.

The complementary product was isolated just as aconine from the corresponding substance obtained with aconitine, viz., by alkalising with sodium carbonate the liquors from which the benzoic acid had been extracted by ether, evaporation to dryness, extraction of alkaloïdal matter by alcohol, and purification of the varnish-like mass left on evaporation to dryness by chloroform. It constituted a yellowish-white friable varnish, readily soluble in water, alcohol, and chloroform, all but insoluble in ether, and exhibiting so close a resemblance to aconine in every respect, save analytical numbers, that the two bodies could be distinguished in no other way: it reduces Fehling's solution when boiled therewith.

0·2640 gram gave 0·5745 CO_2 and 0·1925 H_2O.

	Calculated.		Found.
C_{26}.....	312	59·20	59·35
H_{41}	41	7·78	8·10
N	14	2·66	—
O_{10}.....	160	30·36	—
$C_{26}H_{41}NO_{10}$	527	100·00	

Converted into mercuriodide, 0·2535 gram gave 0·1600 AgI.

	Calculated for $C_{26}H_{41}NO_{10}$, HI, HgI_2.	Found.
Iodine.....	34·35	34·11

From these numbers it would seem that the saponification of japaconitine is effected in accordance with the equation—

$$C_{65}H_{88}N_2O_{20} + 3H_2O = 2C_7H_6O_2 + 2C_{26}H_{41}NO_{10}.$$

Assuming the existence of the hypothetical parent base, $C_{33}H_{47}NO_{12}$, referred to in § 1, this might be written—

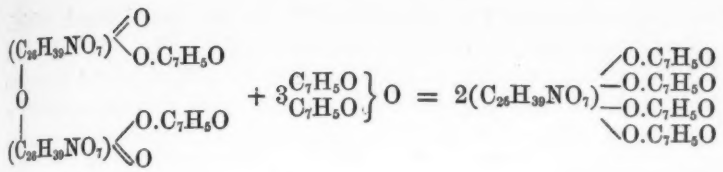
$$(C_{26}H_{39}N.O_7)\begin{cases}=O\\ O.C_7H_5O\\ O\\ (C_{26}H_{39}NO_7)\begin{cases}O.C_7H_5O\\ =O\end{cases}\end{cases} + 3H_2O = 2C_7H_6O_2 + 2(C_{26}H_{39}NO_7)\begin{cases}=O\\ OH\\ OH\end{cases}$$

the parent base being then $(C_{26}H_{39}NO_7)\begin{cases}O.C_7H_5O\\ OH\\ OH\\ OH\end{cases}$.

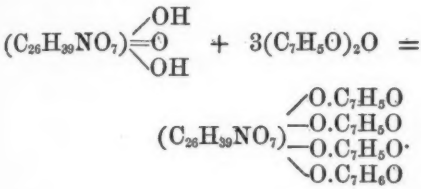
The experiments described in the next section lend considerable support to this view.

§ 4. *Action of Benzoic Anhydride on Japaconitine and Japaconine.*

It has been shown in Parts II and III that by the action of benzoic anhydride on aconitine, aconine, and pseudaconine, dibenzoylated bodies are formed represented in the case of each of the first two substances by $(C_{26}H_{35}NO_7)\begin{cases}O.C_7H_5O\\ =O\\ O.C_7H_5O\end{cases}$ (the products being apparently identical), and by the formula $(C_{27}H_{37}NO_5)\begin{cases}O.C_7H_5O\\ =O\\ O.C_7H_5O\end{cases}$ in the case of pseudaconine; it, therefore, might be supposed that an analogous substance would be formed in the case of japaconitine; on trying the experiment, however, the product was found to be a substance containing *four* benzoyl-groups for every C_{33} in the original japaconitine; viewing japaconitine, as above, as being derived from a parent base $(C_{26}H_{39}NO_7)\begin{cases}O.C_7H_5O\\ OH\\ OH\\ OH\end{cases}$ by dehydration, the tetrabenzoylated body may be represented as being $(C_{26}H_{39}NO_7)\begin{cases}O.C_7H_5O\\ O.C_7H_5O\\ O.C_7H_5O\\ O.C_7H_5O\end{cases}$, formed by the direct addition of benzoic anhydride to japaconitine, thus:—



Moreover, the same tetrabenzoylated derivative appears to be produced when benzoic anhydride acts on japaconine, the reaction then being:—



Japaconitine was heated to 100° for eight hours with twice its weight of benzoic anhydride, containing a small amount of fluid impurities, which rendered it liquid at 100°. On adding alcohol to the product and then agitating with a large bulk of ether and some aqueous tartaric acid, a solution of an alkaloïdal tartrate was formed, the benzoic acid and impurities present and the excess of anhydride remaining unchanged being retained in solution in the ether. From the tartrate thus obtained, alkalis threw down white flakes, readily soluble in ether, but not crystallising distinctly from that menstruum. Of these,

0·2770 gram dried at 100° gave 0·6825 CO_2 and 0·1685 H_2O.

	Calculated.		Found.
C_{54}	648	67·43	67·20
H_{59}	59	6·14	6·75
N	14	1·46	—
O_{15}	240	24·97	—
$(C_{26}H_{39}NO_7)(O.C_7H_5O)_4$	961	100·00	

On saponification, 0·4690 gram of this base gave 0·2415 gram of benzoic acid, containing a little resinous matter; on titration this neutralised soda equivalent to 0·235 $C_7H_6O_2$.

	Calculated.	Found. By weighing.	Found. By titration.
Benzoic acid	50·78	51·49	50·11

This benzoylated derivative did not crystallise from alcohol or ether, nor did it form readily crystallisable salts with acids. On stirring

with dilute nitric acid, a very insoluble nitrate was formed, which appeared indistinctly crystalline under the microscope. It exhibited close similarity to benzoyl apo-aconitine; in a capillary tube it began to soften between 130° and 140°, but did not melt thoroughly until a temperature higher than 160° was attained, no distinct melting point being noticeable.

In order to see if the same substance is obtainable on benzoylating japaconine, this base was treated with benzoic anhydride, &c., just as above described; this base finally obtained perfectly resembled that from japaconitine in all respects.

0·2360 gram gave 0·581 CO_2 and 0·145 H_2O.

	Calculated.	Found.
Carbon.....	67·43	67·11
Hydrogen	6·14	6·82

0·4860 gram, saponified with alcoholic potash, gave 0·2540 gram of benzoic acid containing a little resinous matter; on titration, this neutralised alkali equivalent to 0·2470 $C_7H_6O_2$.

	Found.	
Calculated.	By weighing.	By titration.
50·78	52·26	50·82

A marked difference thus exists between japaconitine and aconitine, in that the latter forms on benzoylating only a dibenzoyl derivative; whilst the former gives a tetrabenzoyl derivative (per C_{33} in each case).

§ 5. *Noncrystalline Alkaloïds of Japanese Aconite Roots.*

The mother-liquors left on crystallising from ether the crude japaconitine obtained as above described closely resembled the corresponding substance obtained from *A. Napellus* roots (Parts I and III); the varnish thus obtained from the first batch of roots worked up gave the following numbers:—Carbon, 67·69; hydrogen, 7·75; nitrogen (by soda lime), 3·23; whence, as with *A. Napellus*, a base was apparently present of lower molecular weight than japaconitine, and containing a higher percentage of carbon. No crystalline substance could be obtained from either this specimen of varnish or the similar substance obtained from either of the other two batches of roots examined.

The alkaline liquors, from which all alkaloïds soluble in ether had been washed out by repeated treatment with that menstruum, still contained a considerable amount of alkaloïdal matter, precipitable by mercuriodide of potassium. On treating the precipitate suspended in alcohol with sulphuretted hydrogen, evaporating, dissolving in water, and precipitating with sodium carbonate, a large quantity of flocculent

basic matter was thrown down apparently identical with the amorphous base from the ethereal mother-liquors of japaconitine; the sodium carbonate filtrate, on evaporation to dryness and treatment with alcohol yielded a small quantity of amorphous basic matter, insoluble in water, with some amount of a base readily soluble in water and chloroform, and apparently identical with japaconine. The quantity of amorphous alkaloïd obtained from the mercuriodide precipitate corresponded to about 20 grams, or 0·14 per cent. of the weight of the roots employed, and hence was nearly equal to the amorphous alkaloïds obtained from the ethereal mother-liquors.

In each case examined, all the crystallisable alkaloïd present in the concentrated extract obtained from the roots was dissolved out by four or five successive treatments with ether; the amorphous base or bases present appear to be retained in alkaline fluids much more energetically than japaconitine, so that prolonged treatment with ether fails to dissolve out the whole, although a portion is thus extracted. In this respect the amorphous bases resemble morphine when dissolved in caustic potash, or cotarnine dissolved in sodium carbonate or dilute caustic soda; agitation with ether (and certain other solvents) then only removes a fraction of the dissolved alkaloïd.

Appendix.

By C. R. Alder Wright and A. E. Menke, Daniell Scholar, King's College.

The results above described indicate that each of the two different batches of Japanese aconite root examined contained one and only one crystallisable alkaloïd, the substance finally obtained being in every case identical, no matter which batch or what fraction was examined. In each instance the roots were originally worked up by percolation with alcohol acidulated with tartaric acid in the proportion of one part of acid to 100 of root; it would seem *à priori* not at all impossible that the tartaric acid thus introduced might act on the alkaloïd during the evaporation down of the alcoholic percolate, the result probably being (judging from the action of tartaric acid on aconitine and pseudaconitine) removal of the elements of water without any saponification being effected; in other words, it is not unlikely that the roots originally contained what has been above referred to as the "hypothetical parent base," $C_{33}H_{47}NO_{12}$, and that this became dehydrated forming $C_{66}H_{88}N_2O_{21}$, its sesqui-apo-derivative, during the process of extraction.

In the hope of isolating the unaltered base, $C_{33}H_{47}NO_{12}$, probably originally present, a third batch of roots was worked up, but without any acid at all being employed to acidulate the alcohol used; 1 cwt. of

roots (about 50 kilos.) were percolated by Messrs. Hopkins and Williams with plain alcohol; the percolate, condensed to about $1\frac{3}{4}$ gallons by evaporation, was sent to us and the alkaloïds contained isolated as described above, viz., by exposure to air for some days to remove most of remaining alcohol, addition of water, filtration, treatment with sodium carbonate and ether, and agitation of the ethereal extract with tartaric acid solution. From the crude tartrates thus obtained, the crystallised base was isolated by treatment with soda and ether, spontaneous evaporation, and separation of the crystals thus produced from the resinoid base accumulating in the mother-liquors by filter-pumping and washing with ether. After methodical crystallisation, there were ultimately obtained about 50 grams of crystallised base and 55 grams of resinoid base from the mother-liquors, or about 0·10 per cent. of crystals and 0·11 per cent. of varnish-like bases, or 0·21 per cent. in all. As previously indicated by Paul and Kingzett, and as found with the first batch examined, this yield is considerably superior to that obtained with a good sample (2 cwts.) of *A. Napellus* roots (Part I), which gave about 0·03 per cent. of crystallised aconitine and 0·04 per cent. amorphous bases, or 0·07 per cent. in all of alkaloïds soluble in ether. From these results, it may be fairly inferred that the Japanese roots are considerably richer in crystallisable as well as total alkaloïds than ordinary *A. Napellus* roots; whence, since the action of japaconitine on the skin appears to be much the same as that of aconitine and pseudaconitine, it seems highly probable that the Japanese roots will prove a more convenient source of crystallisable definite active alkaloïds than the roots now ordinarily used, the more so as japaconitine is more easily separable from the amorphous bases than is the case with pseudaconitine, which appears at present to be the active constituent of most of the commercial so-called "aconitine."*

The crystals that were thus obtained were got in three different fractions, as follows:—By spontaneous evaporation until about three-quarters of the crystallisable alkaloïd present had separated, filter-pumping, and washing with ether, a mass of crystals was obtained almost free from amorphous bases. This was dissolved in tartaric acid, precipitated with a slight excess of clear caustic soda solution, and agitated with ether sufficient to dissolve only about a quarter of the precipitate, which quickly became a mass of crystals. The whole was then filter-pumped and the residue washed with ether, and finally several times with water to remove soda salts; the crystals thus left were marked A. The ethereal solution thus filtered from A gave on spontaneous evaporation a crop of crystals (B), identical in all respects

* Dr. T. R. Fraser, of Edinburgh, has kindly undertaken the comparative examination of the physiological action of aconitine, pseudaconitine, japaconitine, and some of their derivatives.

with A. Finally, the ethereal mother-liquors from which the original mass of crystals had separated, deposited on standing a further quantity of crystals with much viscid alkaloïd; by thinning with ether and filter-pumping, the crystals were mostly separated from the amorphous alkaloïd; the crystals were finally purified by rubbing with dilute warm nitric acid, which at first dissolved them, and then deposited a crystalline nitrate. From this crystallised salt, drained on the pump-filter, and washed with dilute nitric acid, the base was isolated by soda and ether, and the crystals thus obtained were marked C.

A fourth specimen of crystals (D) was obtained as follows:—In order to see whether all the crystallisable alkaloïds can be practically removed from the ground roots by alcohol alone, the marc practically exhausted by plain alcohol was treated by Messrs. Hopkins and Williams with a further quantity of alcohol, slightly acidulated with sulphuric acid (about 30 grains of concentrated acid per gallon); the percolate was evaporated down to about a gallon, and sent to us for examination. On treatment in the same way as the first percolate with plain alcohol, it was found, firstly, that only a small quantity of resinous matter was present; wherefore the plain alcohol first used had evidently dissolved out practically all the resinous matter from the roots. Secondly, the total amount of alkaloïds soluble in ether after repeated treatments only amounted to between 2 and 3 grams, of which about half was crystalline and half amorphous; the crystals left on separation by the filter-pump and washing with ether were recrystallised from ether, and thus formed specimen D, identical in all respects with A, B, and C. It is thus evident that alcohol alone, without addition of any acid, will suffice to remove practically all the alkaloïds contained in Japanese roots (and presumably, therefore, also in *A. Napellus* and *A. Ferox* roots). It is noticeable that the condensed percolate obtained with plain alcohol was distinctly acid to test paper; whence, since inorganic acids are apt to decompose and saponify the aconite alkaloïds, and tartaric acid to dehydrate them, it appears to be preferable to exhaust aconite roots with plain alcohol rather than with acidulated alcohol in manufacturing the pure crystallised alkaloïds, which it is to be hoped will speedily supersede the amorphous and unreliable preparations of very variable potency now met with commercially under the name of (so-called) "aconitine."

The following numbers were obtained with these four specimens, A, B, C, and D. In each case the corrected melting point was almost exactly the same as that previously found with the other specimens; A and C melted at 185·5°, B at 183°, and D at 181°: the small quantity of specimen D obtained, and the consequent difficulty in thoroughly purifying is evidently the cause of the somewhat low melting point found.

(A.) 0·2640 gram gave 0·6165 CO_2, and 0·1790 H_2O.
0·4090 „ burnt with soda lime gave by titration 0·00938 nitrogen; by conversion into Pt salt 0·0605 Pt.
0·7170 gram gold salt gave 0·1495 Au.
(B.) 0·3325 „ gave 0·7750 CO_2, and 0·2250 H_2O.
(C.) 0·3700 „ gave 0·8620 CO_2, and 0·2550 H_2O.
0·6420 „ gold salt gave 0·1320 Au.
(D.) 0·3675 „ gave 0·8570 CO_2, and 0·2540 H_2O.

	Carbon in base.	Hydrogen.	Nitrogen.	Gold in gold salt.
(A)	63·69	7·53	2·29 2·09	20·85
(B)	63·57	7·52	—	—
(C)	63·54	7·66	—	20·56
(D)	63·60	7·68	—	—
Average of 7 specimens examined previously	63·58	7·50	2·27	20·43
Calculated for $C_{66}H_{88}N_2O_{24}$	63·67	7·07	2·25	20·39

It is hence evident, firstly, that only one crystallisable alkaloïd was contained in this third batch of roots; secondly, that this alkaloïd was identical with that contained in the two batches of root previously examined, and thirdly, that precisely the same substance resulted whether the alcohol employed were acidulated with tartaric acid or not: in other words, that if, as is probable, the roots originally contain an alkaloïd $C_{33}H_{47}NO_{12} = (C_{26}H_{39}NO_7)\begin{matrix}O.C_7H_5O\\OH\\OH\\OH\end{matrix}$, this becomes dehydrated to the sesqui-apo-derivative termed above japaconitine, and indicated by the formula—

$$(C_{26}H_{39}NO_7)\begin{matrix}O.C_7H_5O\\O\end{matrix}$$
$$\Big|$$
$$O$$
$$\Big|$$
$$(C_{26}H_{39}NO_7)\begin{matrix}O\\O.C_7H_5O\end{matrix}$$

by the heat alone employed in evaporating off the alcohol, even if no tartaric acid at all be employed to acidulate the alcohol.

The non-crystalline bases accumulating in the ethereal mother-liquors of the first rough crystals of japaconitine obtained from this batch were examined with the following results. Carbon = 65·73, hydrogen = 8·07, nitrogen = 2·69 per cent.: benzoic acid formed on saponification with alcoholic potash = 19·1 per cent. After saponi-

fication, the base produced was almost wholly dissolved by water, and closely resembled aconine. From these results, it seems to follow that the amorphous base was almost wholly of the saponifiable class, and closely related to japaconitine; in which respect it seems to differ somewhat from the amorphous bases obtained from *A. Napellus* (Parts I and III), which yielded much less benzoic acid on saponification, and therefore presumably contained a large admixture of a non-saponifiable alkaloïd.

In conclusion, the following deductions may be drawn from the preceding experiments:—

(1.) The aconite roots imported from Japan appears to be tolerably uniform in character, and considerably richer in active crystallisable alkaloïds, as well as in the non-crystalline bases, than *A. Napellus* root.

(2.) The active crystallisable alkaloïd present is, as supposed by Paul and Kingzett, different from both aconitine and pseudaconitine, although closely allied to both, and especially to the former.

(3.) Only one crystallisable alkaloïd could be isolated from each of three different batches of roots examined; this alkaloïd is indicated by the formula $C_{66}H_{88}N_2O_{21}$ (and not by the approximate formula attributed by Paul and Kingzett, $C_{29}H_{43}NO_9$).

(4.) This alkaloïd, to which it is proposed to give the provisional name *japaconitine*, breaks up on saponification into benzoic acid, and a new base *japaconine*, $C_{26}H_{41}NO_{10}$; on treatment with benzoic anhydride, it forms a derivative containing four benzoyl groups for every C_{33} originally present, in this respect differing from aconitine, which only forms a dibenzoylated derivative on similar treatment. The same derivative is formed on benzoylating japaconine. Japaconitine and japaconine very closely resemble aconitine and aconine respectively in all their physical properties, so that save in analytical numbers and by benzoylating, their discrimination is almost impracticable.

(5.) Contrary to the statements of Paul and Kingzett, japaconitine readily forms crystallisable salts, especially with nitric, hydrochloric, and hydrobromic acids; the hydrobromide, like that of aconitine, contains $2\frac{1}{2}$ H_2O for every C_{33} present.

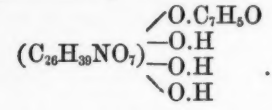
(6.) In isolating japaconitine from the roots, plain alcohol may be used instead of alcohol acidulated with tartaric acid (or with a mineral acid); practically all the alkaloïd present is thus easily extracted. Probably the same remarks apply to other kinds of aconite roots, wherefore in all probability it is better in such cases to use plain alcohol only for the purpose of extracting the alkaloïds.

(7.) The relationships of japaconitine to its derivatives and to aconitine are conveniently expressed by regarding japaconitine as being formed by the sesqui-dehydration of an alkaloïd, $C_{33}H_{47}NO_{12}$

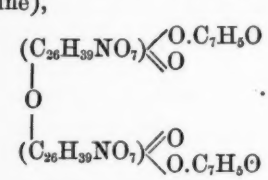
(not yet isolated in an unaltered state), closely related to aconitine, as indicated by the following table:—

Japaconitine Series.

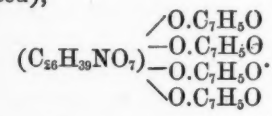
Hypothetical parent base,



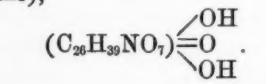
Sesqui-apo-derivative (japaconitine),



Benzoyl-derivative (tetrabenzoylated),



Saponification product (japaconine),



Aconitine Series.

Aconitine,

Apo-derivative (apo-aconitine),

Benzoyl-derivative (dibenzoylated),

Saponification product (aconine),

Apo-aconine,

XLVI.—*The Alkaloïds of the Veratrums.* Part II. *The Alkaloïds of Veratrum Album.*

By C. R. Alder Wright, D.Sc. (Lond.), and A. P. Luff.

§ 1. *Isolation of Constituent Alkaloïds.*

Although numerous chemists and pharmacists have partially examined the alkaloïds contained in *Veratrum album* and other allied species (*V. viride*, *V. Lobelianum*, &c.), yet very little exact knowledge has been gained as to the chemical characters of the bodies isolated, whilst in many cases the identity and homogeneity of the educts obtained are open to considerable doubt, no analyses having been made of them.

In 1819 Pelletier and Caventou (*Ann. Chim. Phys.* [2], **14**, 69), obtained from *V. album* roots a sternutatory alkaloïdal body, which they appear to have regarded as identical with the so-called "veratria" from *V. Sabadilla* seeds, and also with the active principle of *Colchicum Autumnale*. E. Simon showed in 1837 (*Pogg. Ann.*, **41**, 569), that besides so-called "veratria," *V. album* contains a base to which he applied the name *jervine*, readily crystallisable from alcohol, and characterised by forming a very insoluble sulphate: this "jervine" was analysed by Will (*Ann. Chem. Pharm.*, **35**, 116), who obtained the following numbers (recalculated from the original data):—

Water of crystallisation in crystallised base.	6·88	6·88
Carbon in base dried at 100°	74·91	74·55
Hydrogen „ „	9·57	9·74
Nitrogen (estimated by volume)	5·38	
Platinum in platinum salt	14·33	14·55

from these numbers he deduced the formula $C_{60}H_{45}N_2O_5$ (C = 6, O = 8), for which latter chemists, following Gerhardt, have substituted $C_{30}H_{46}N_2O_3$.

This same non-sternutatory crystallisable base has also been regarded by Peuguet, C. L. Mitchell and others, as existing in *V. viride*, whilst recently Tobien has stated (Inaugural Dissertation, Dorpat, 1877; *Pharm. J. Trans.*, April 13, 1878, p. 808) that it is also contained in *V. Lobelianum*. Tobien's analyses, however, led him to a formula considerably different from that deduced from Will's numbers, viz., to $C_{27}H_{47}N_2O_8$, the hydrochloride being $C_{27}H_{47}N_2O_8$, HCl.

The identity of the "jervine" from *V. viride* with Simon's base, on the other hand, has been denied by Bullock and others, by some of

whom the term *viridine* has been applied to the crystallisable alkaloïd from *V. viride:* as, however, few if any of the observers who have worked on the subject have operated in such a way as to inspire confidence in the purity and homogeneity of their products, and as more especially the substances examined have, as a rule, neither been analysed nor separated into fractions of constant character, or otherwise treated so as to exclude the possibility of their being mixtures of several substances, it is evident that the relationship of the crystallisable alkaloïdal constituents of these different species is still an open question; whilst the results obtained in Part I with *V. Sabadilla* render it not improbable that the so-called "veratria" of *V. album* (termed veratralbine by some), and that of *V. viride* (sometimes distinguished as veratroïdine) may be mixtures of more than one difficultly crystallisable or non-crystalline base.

To throw some light on this question, 27 lbs. (about 12 kilos.) of crushed dried roots of *V. album* obtained from Messrs. Hopkin and Williams were percolated with 4 gallons of alcohol containing 60 grams of tartaric acid (0·5 per cent. of the weight of the roots), and several gallons more unacidulated alcohol, the percolators being worked in series, so that the weak liquor from a partially exhausted batch was used to wash a newer one, and so on, the object being to obtain as concentrated a liquor as possible, and so to introduce less chance of alteration by continued exposure to heat on evaporating off the alcohol. The percolate concentrated to a small bulk by distillation was then mixed with water, strained from the resin that separated, rendered slightly alkaline with caustic soda, and shaken many times with about its own bulk of ether, the ethereal solution being separated and shaken with aqueous tartaric acid, and the ether then used over again, so that an acid solution of tartrates of alkaloïds was thus obtained, whilst resinous matters, &c., remained dissolved in the ether. After some seven or eight treatments with ether scarcely any appreciable amount of alkaloïdal matter was further taken up by the ether, nor was any dissolved by fusel oil; a notable quantity of a brown flocculent alkaloïdal substance was, however, suspended in the aqueous liquid: this was collected on a calico filter, and purified by solution in acetic acid, filtration from undissolved resinous matter, and precipitation by soda; the gelatinous brownish precipitate obtained, when drained, washed, and dried, dissolved in boiling alcohol with the exception of some humus-like flakes insoluble in acids; the filtered solution deposited nearly white crystals on cooling, the mother-liquors of which gave a little more on spontaneous evaporation, with a small quantity of amorphous basic matter readily soluble in cold alcohol. These crystals are hereafter referred to as *fraction* 1.

The crude acid tartrate solution obtained from the first ethereal

extract was then precipitated by caustic soda and shaken again with fresh ether in much smaller quantity than at first; a portion thus dissolved, whilst a considerable amount remained insoluble even after two or three such treatments with ether: to remove all the more soluble constituents mechanically retained, the undissolved portion was dissolved in tartaric acid and treated again with soda and ether; the substance then left undissolved is referred to as *fraction* 2. The ethereal solutions thus obtained deposited on spontaneous evaporation a quantity of crystals, *fraction* 3, the mother-liquors of which dried up to a honey-like viscid mass, *fraction* 4.

In this way a first rough separation of alkaloïdal constituents was effected, based on their differing solubilities in ether, or in ether containing resinous matters, more soluble alkaloïds, &c., in solution. Fractions 1, 2, and 3 were crystalline to a greater or lesser extent, whilst fraction 4 was wholly amorphous; this last fraction contained the whole of the sternutatory alkaloïdal constituents, none of the first three producing the peculiar provocation to sneeze characteristic of "veratria."

On further working up these different fractions, it was found that although no one of them was pure and homogeneous, in each a different alkaloïd predominated. Fraction 1 consisted almost entirely of a well crystallised alkaloïd, $C_{29}H_{43}NO_7$, which we propose to term, provisionally at least, *pseudojervine*, inasmuch as whilst it resembles jervine in several respects, it differs therefrom notably in many points. Fraction 2 contained some pseudojervine and some jervine (which when pure we find to be indicated by $C_{26}H_{37}NO_3$), but chiefly consisted of an amorphous base, probably indicated by the formula $C_{28}H_{43}NO_5$. Fraction 3 consisted of jervine, with a small quantity of a third crystallisable base, $C_{26}H_{43}NO_2$, giving a colour reaction with sulphuric acid quite different from that of jervine; whilst fraction 4 contained a minute quantity of jervine, and at least two uncrystallisable alkaloïds, one of which, present only in small quantity, is the chief sternutatory ingredient, and is very probably identical with the veratrine (of Couerbe) from *V. Sabadilla*, as it yields veratric acid on saponification, whilst the other is the amorphous base just referred to as probably indicated by $C_{29}H_{43}NO_5$. The total quantity of alkaloïdal matters obtained from the 12 kilos. of roots employed was about 50 grams or 0·42 per cent. Of this, rather more than one-half consisted of non-crystalline bases, the sternutatory product constituting fraction 4 weighing some 6—7 grams, and the amorphous base of fraction 2 nearly 20 grams. The total jervine present was about 16—17 grams, that of pseudo-jervine being 4—5 grams, whilst about 3 grams of the third crystallisable base (which we propose to term *rubijervine*) were present. As, however, these bases were more or less intermixed in the different frac-

tions, the quantities of pure substances ultimately separated from one another were by no means equal to the total quantity present.

§ 2. *Examination of Fraction* 3.

The results obtained by the further examination of this fraction are first described, as they throw light on those obtained with the other fractions. The crystals that separated from ether as just described, when well washed with ether were but very sparingly soluble in that menstruum, although they dissolved far more readily in ether already containing in solution the amorphous bases constituting fraction 4. As a first preliminary trial these crystals were analysed along with those obtained by recrystallising fraction 1, when the following numbers and properties were observed, clearly showing non-identity:—

	Fraction 1.	Fraction 3.
Water of crystallisation in air-dry crystals	0·92	5·81 5·27
Carbon in base dried at 100°	67·86	75·99
Hydrogen	8·75	10·09
Melting point (corrected)	280°	231°
Effect on stirring with dilute sulphuric acid.	Dissolved to a clear solution depositing crystals on standing, which after separation from the excess of acid by the filter-pump, were very sparingly soluble in cold water, but readily soluble in boiling water.	Did not dissolve, but became an indistinctly crystalline semi-gelatinous magma, which after separation from the excess of acid by the filter-pump, were as good as insoluble in water, whether cold or boiling. The acid filtrate contained a little of a different base (rubijervine).

Fraction 3 accordingly agrees in general characters and analytical numbers sufficiently well with Simon's jervine to indicate that the same alkaloïd in a more or less pure state constituted the majority both of Simon's product and of fraction 3,—whilst fraction 1 chiefly consisted of a wholly different alkaloïd.

In order to obtain the constituents of fraction 3 as pure as possible in a separate condition, the crystals from ether were digested with warm dilute sulphuric acid, and the semi-gelatinous magma thoroughly drained and washed, and then suspended in boiling water and again filtered. This last filtrate contained scarcely any appreciable amount

in solution, clearly showing that the alkaloïdal sulphate is very sparingly soluble, even in boiling water. From this insoluble sulphate the base was regenerated by boiling with alcohol and sodium carbonate. The filtered liquid deposited, on cooling, light white flaky crystals, which yielded the following numbers:—

Specimen I.—Base prepared as just described and crystallised from alcohol.

0·5165 gram of air-dry base lost at 100° 0·0325 gram.
0·256 gram of dried base gave 0·709 CO_2 and 0·220 H_2O.

Specimen II.—Specimen I again converted into sulphate by rubbing in a mortar with dilute sulphuric acid, and after filtration and washing regenerated by means of sodium carbonate and alcohol (no more than traces of base soluble in sulphuric acid were thus separated).

0·4850 gram of air-dry crystals lost at 100° 0·0360 gram.
0·2575 „ of base dried at 100° gave 0·7150 CO_2 and 0·219 H_2O.
0·399 „ burnt with soda lime gave by titration 0·0133 nitrogen, by conversion into platinum salt, 0·093 Pt.

Specimen III.—Obtained by spontaneous evaporation from the mother-liquors of Specimen II.
0·3740 gram lost at 100° 0·0255.

These numbers agree with the formula $C_{26}H_{37}NO_3,1\frac{1}{2}H_2O$, but it is highly probable that the crystals really contained $2H_2O$, and that the deficiency in water of crystallisation is due to separation of a little anhydrous base from hot or strong alcohol (*vide infra* § 4).

	Calculated for $C_{26}H_{37}NO_3,1\frac{1}{2}H_2O$.	Calculated for $2H_2O$.	Found. I.	Found. II.	Found. III.
Water.....	6·16	8·05	6·29	7·42	6·82

	Calculated.		Found. I.	Found. II.	
C_{26}	312	75·91	75·53	75·73	
H_{37}	37	9·00	9·54	9·45	
N.....	14	3·41	—	3·33	3·29
O_3.....	48	11·68	—	—	
	411	100·00			

The gold salt gave the following numbers. It was precipitated from a solution of the base in highly diluted hydrochloric acid by addition of gold chloride, and was distinctly crystalline, only becoming anhydrous at 100° slowly.

0·428 gram of air-dry salt lost at 100°, 0·0125 ..... = 2·92
Calculated for $C_{26}H_{37}NO_3$, HCl, $AuCl_3$, H_2O ..... = 2·34
0·4155 gram of dried salt gave 0·1065Au ..... = 25·63
Calculated for $C_{26}H_{37}NO_3$, HCl, $AuCl_3$.. ..... = 26·13

On rubbing the base with dilute hydrochloric acid, a magma of crystals resulted, only very sparingly soluble in water even when boiling, the solubility being diminished by the presence of free hydrochloric acid. In acetic acid it dissolved, the solution yielding with potassium nitrate solution a very insoluble precipitate of nitrate.

The corrected melting points of the different specimens of base were found to be—

Specimen I..... 231°, with slight previous browning,
„ II..... 237°; no previous browning,
„ III..... 231°; slight previous browning,

the fused mass being in each case much darker than the original substance, being distinctly browned.

The base $C_{26}H_{37}NO_3$ thus obtained agreed well in all its characters with the "jervine" of Simon and Will; moreover, it yielded with cold strong sulphuric acid the peculiar colour reaction usually ascribed to jervine, viz., dissolving to a yellow fluid, which speedily becomes successively dark yellow, brownish-yellow, and the peculiar greenish-brown tint obtained when a somewhat stale solution of potassium ferricyanide is mixed with ferric chloride. After standing some little time, dependent on the humidity of the atmosphere, &c., a green tint is developed; when only a speck of crystallised base is used, and a drop or two of acid in a white porcelain basin, the green appears first at the edges, and extends until the whole is a dark green. Large quantities in a test-tube do not become green until after some hours' standing, but the green shade is immediately developed on very slightly diluting with water the greenish-brown fluid formed after standing for half-an-hour or so, the tint becoming successively olive-green, dark chrome-green, and finally dark emerald, as the addition of water progresses. With more water the tint becomes lighter, until finally a nearly colourless fluid results, with a few brownish-yellow flakes suspended therein. This peculiar colour reaction, however, is not confined to jervine, the pseudojervine described below also yielding just the same tints, whilst the other alkaloïdal constituents give with cold sulphuric acid yellow solutions, becoming quickly brown-yellow, brown, reddish-brown, and finally more or less red in tint, in this respect being more analogous to veratrine and cevadine (Part I), which form with sulphuric acid yellow solutions, gradually changing to dark yellow, brownish-yellow, chestnut, dull scarlet, and deep blood-red. These

two last alkaloïds are indistinguishable from one another by transmitted colour only, but are differentiated in that cevadine gives a dark green-fluorescent red solution, whilst veratrine (of Couerbe) gives no fluorescence. On standing some hours so as to absorb moisture, or on adding to the blood-red solution a minute quantity of water, the colour changes in each case to a lovely crimson or magenta shade, permanent for many weeks.

The acid filtrate from the jervine sulphate obtained on first treating fraction 3 with dilute sulphuric acid was found to contain an alkaloïd wholly different from jervine, though probably closely allied thereto. The liquid was treated with a slight excess of caustic soda, and the precipitate drained and washed. In this state it dissolved wholly in a few drops of dilute sulphuric acid, leaving no trace of jervine sulphate undissolved. The solution deposited crystals on standing, readily soluble in hot water, or in cold water acidulated with sulphuric acid, but less easily dissolved by cold water free from acid. The free base after crystallisation from alcohol was anhydrous. In dilute hydrochloric acid it readily dissolved, a magma of crystals readily soluble in water being formed when a drop or two of somewhat stronger acid was used instead of dilute acid. With concentrated sulphuric acid it dissolved to a clear yellow fluid, becoming successively dark yellow, brownish-yellow, and brownish blood-red, changing after several hours to a brownish-purple. On diluting slightly with water the brownish blood-red liquid, it became successively crimson, purple, dark lavender, dark violet, and ultimately light indigo.

The following numbers were obtained :—

0·2330 gram of base dried at 100° gave 0·6620 CO_2 and 0·2285 H_2O.
0·3520 „ „ burnt with soda-lime gave by titration 0·01165 gram N, and by platinum salt 0·0835 Pt.

	Calculated.		Found.	
C_{26}	312	77·81	77·48	
H_{43}	43	10·72	10·89	
N	14	3·49	3·31	3·38
O_2	32	7·98	—	
$C_{26}H_{43}NO_2$....	401	100·00		

The gold salt formed a light yellow, indistinctly crystalline, insoluble precipitate, of which—

0·2215 gram dried at 100° gave 0·0595Au.. = 26·86 per cent.
Calculated for $C_{26}H_{43}NO_2$, HCl, $AuCl_3$ .. = 26·49 „

The crystallised base melted at almost exactly the same temperature as jervine, 236° being the corrected melting point obtained with the purest crystals, and 228° that with a small quantity of less pure

crystals obtained by spontaneous evaporation from their alcoholic mother-liquors.

From the probable connection between this base and jervine suggested by their occurrence together and not widely different formulæ, together with the difference in colour-reaction with sulphuric acid, we propose to distinguish the base $C_{26}H_{43}NO_2$ provisionally as *rubijervine*, *i.e.*, the jervine-like alkaloïd which gives a *red* colour with sulphuric acid.

When perfectly free from other alkaloïdal matter more readily soluble in ether, neither jervine nor rubijervine are easily dissolved by that menstruum, although a little of each is taken up on shaking therewith a solution of any salt and a little caustic soda; if, however, they be mixed with the more soluble alkaloïds constituting fraction 4, ether dissolves them much more freely. This is also the case with pseudojervine; but under any circumstances the solubility of this latter in ether is much less than that of either jervine or rubijervine.

§ 3. *Examination of Fraction* 1.

The crude crystals, obtained as above described, when recrystallised from hot alcohol formed a snow-white mass much resembling jervine in appearance, but melting at a much higher temperature (280° corrected), and giving with cold concentrated sulphuric acid a succession of colours nearly the same as those yielded by a specimen of pure jervine tested side by side, but exhibiting in certain stages a redder or browner shade, suggesting that with a body giving the colour reaction of jervine, a small quantity of something else giving a red colour was intermixed (presumably rubijervine); this was subsequently found to be actually the case.

On treatment with warm considerably dilute sulphuric acid, these crystals almost wholly dissolved, leaving behind only a minute quantity of jervine sulphate; the solution on standing deposited crystals which, when drained from the acid mother-liquor, were only sparingly soluble in cold water, but readily soluble in hot water. The solution of sulphate thus practically freed from jervine was precipitated by soda, and the washed and drained precipitate stirred up with dilute hydrochloric acid in very slight excess: a crystalline magma was thus formed, which, after draining from the acid liquor, was only sparingly soluble in water, even when hot, but was much more readily dissolved in water slightly acidulated with hydrochloric acid. The hydrochloride left undissolved by washing with hot water, was boiled with alcohol and sodium carbonate, and the base which crystallised from the alcoholic liquors again converted into hydrochloride and filter-pumped to free from any possibly adherent traces of any other base yielding a more soluble hydrochloride, but mechanically retained. By

means of alcohol and sodium carbonate, the base was finally regenerated from the hydrochloride, and obtained in crystals much resembling jervine in appearance, and now yielding precisely the same colour-reaction with sulphuric acid.

These crystals were anhydrous when air-dry, and melted at 299° (corrected), browning during fusion, but not perceptibly previously. The following numbers were obtained :—

I. Purest base obtained as just described—

0·2045 gram gave 0·161 H_2O and 0·505 CO_2.
0·3325 gram, burnt with soda-lime, gave 0·065 Pt.

II. Specimen of base still retaining a minute quantity of rubijervine (after treatment with sulphuric acid to separate jervine, but before conversion into hydrochloride to separate rubijervine)—

0·258 gram gave 0·642 CO_2 and 0·208 H_2O.

	Calculated.		Found.	
			I.	II.
C_{29}	348	67·31	67·35	67·86
H_{43}	43	8·32	8·75	8·95
N	14	2·71	2·77	—
O_7	112	21·66		
$C_{29}H_{43}NO_7$ ..	517	100·00		

0·1925 gram of gold salt from Specimen 1, dried at 100°, gave 0·0445 Au = 23·11 per cent.
Calculated for $C_{29}H_{43}NO_7$, HCl, $AuCl_3$ = 22·90 per cent.

The crystalline hydrochloride, when air-dry, contained $C_{29}H_{43}NO_7$, HCl, $2H_2O$; 0·4115 gram dried at 100° lost 0·0325 gram = 7·90 per cent.
Calculated = 6·10 per cent.

From the partial similarity of this base to jervine, we propose to term it *pseudojervine*. The mother-liquors from which the crystalline hydrochloride of pseudojervine was separated, as just described, were precipitated with caustic soda, drained, and washed, and then rubbed with a slight excess of hydrochloric acid: some little quantity of pseudojervine hydrochloride was thus obtained in crystals; the slightly acid liquid drained from this contained too little alkaloïd in solution to permit of a perfect separation of pure rubijervine from it; but that this base was actually present in small quantity is clearly indicated by the following numbers obtained on analysis of the mixture of pseudojervine and rubijervine precipitated therefrom by soda and crystallised from a small bulk of alcohol :—

	Pseudojervine.	Rubijervine.	Mixed bases examined.
Carbon in free base.....	67·31	77·81	69·85
Hydrogen in free base	8·32	10·72	9·60
Gold in gold salt.....	22·90	26·49	24·48
Melting point (corrected)	299°	236°	268°

and also by the circumstance that the series of colours given with sulphuric acid by this mixture was indistinguishable from that yielded by a mixture of pure pseudojervine and rubijervine in which the former somewhat preponderated.

From these results it is evident that fraction 1 consisted essentially of pseudojervine, a minute quantity of jervine and of rubijervine being also present; the much less solubility in ether (containing more soluble alkaloïds, resinous matters, &c.) of pseudojervine than of the other two bases is thus rendered evident, fraction 1 being the portion left undissolved by ether after many treatments therewith, whilst fraction 3 consisted of that portion of the crystallisable alkaloïds present which were most readily dissolved by ether, having been taken up by that solvent in two successive treatments therewith.

§ 4. *Examination of Fraction* 2.

From the foregoing results it is evident that this fraction might, *à priori*, be expected to contain quantities of jervine, pseudojervine, and rubijervine intermediate between those found in fractions 1 and 3, *i.e.*, that there would be present some considerable amount of jervine, a little pseudojervine, and some little rubijervine. These bodies were actually found to be present, but, in addition, a considerable amount of an amorphous base was also present, the solubility of which in ether, though sufficiently great to prevent any large quantity being found in fraction 1, was yet sufficiently small to prevent more than a portion of it being taken up on the second treatment with ether performed to separate fraction 2 from fractions 3 and 4.

The whole mass of substance undissolved by ether on the second treatment therewith constituting fraction 2, was warmed with dilute sulphuric acid, allowed to stand 24 hours, and filter-pumped. The filtrate contained a large amount of a readily soluble sulphate (or mixture of sulphates), whilst the residue on the filter consisted of jervine sulphate intermixed with pseudojervine sulphate, and a small quantity of rubijervine sulphate.

The filtrate was precipitated by caustic soda, and the precipitate drained, washed, and dissolved in hot alcohol: after long standing and spontaneous evaporation a few crystals separated, which, after collec-

tion, washing, and recrystallisation, were anhydrous, and gave numbers agreeing with pseudojervine, the melting point being 287°, and the colour-reaction with sulphuric acid almost precisely identical with that of pure pseudojervine tested side by side. The mother-liquors of these few crystals dried up to a varnish which would not yield crystalline salts, and was devoid of sternutatory properties: on analysis this yielded the following percentages:—

Carbon, in base, dried at 100°	69·36
Hydrogen, in base, dried at 100°	9·21
Nitrogen (by soda lime) „	2·86
Gold in gold salt dried at 100°	23·18

These numbers fall somewhat below those calculated for the formula $C_{28}H_{43}NO_5$, which requires carbon, 71·04; hydrogen, 9·09; nitrogen, 2·96; and gold in Au salt, 24·14; but are just those which would be obtained with a mixture of a substance of this composition with a little pseudojervine (containing carbon, 67·31; hydrogen, 8·32; nitrogen, 2·71; gold in Au salt, 22·90): since the varnish-like base from these mother-liquors must necessarily have contained some pseudojervine, whilst the substance described in § 5 (which was doubtless essentially the same body as this amorphous base, but also containing a minute quantity of veratrine) gave numbers approximating to the formula $C_{28}H_{43}NO_5$, it is evident that this formula is at any rate an approximation to the true formula of the amorphous base, which we propose to term (at any rate provisionally) *veratralbine*, this name having been applied by Mitchell and others to the amorphous bases soluble in ether obtained from *V. album*, the which bases as shown in § 5 consist almost entirely of $C_{28}H_{43}NO_5$, the sternutatory properties being due to the presence of a small percentage of veratrine (or at least of a base yielding veratric acid on saponification).

Veratralbine is unchanged by boiling with alcoholic potash for 24 hours: the amorphous mixture of veratralbine and a little pseudojervine, just described, when treated in this way yielded no trace of any kind of acid saponification-product; the residual base formed a gold salt containing 22·91 per cent. of gold; inasmuch as the original substance formed a gold salt containing 23·18 per cent. of Au, it is evident that no diminution in molecular weight took place during the treatment with alcoholic potash.

With sulphuric acid veratralbine gives a series of colours closely akin to those developed by cevadine, and far more resembling those produced by rubijervine than those yielded by jervine or pseudojervine; the solution of a speck of the base in strong sulphuric acid becomes successively yellow, dark-yellow, brownish-orange, and brownish blood-red, with a strong green fluorescence.

The mixture of sulphates left on the filter contained so much pseudojervine that a complete separation of that base by washing with cold water or by regenerating the alkaloïds (by alcohol and sodium carbonate), reconversion into sulphates by dilute sulphuric acid and filtering, appeared to be impracticable; pure jervine sulphate, however, was readily obtained by boiling the mixed sulphates (washed from the majority of the excess of sulphuric acid) with water and filter-pumping hot: by regenerating the base, by means of alcohol and sodium carbonate, jervine was obtained identical with that described above, melting at 239° (corrected) and yielding the following numbers (after drying at 100°) agreeing with $C_{26}H_{37}NO_3$.

0·2195 gram gave 0·6075 CO_2 and 0·182 H_2O.
0·235 „ 0·6465 „ 0·205 „

	Calculated.	Found.	
Carbon	75·91	75·48	75·03
Hydrogen	9·00	9·23	9·69

The colour reaction with sulphuric acid was identical with that yielded by jervine from fraction 3.

Two different specimens of impure jervine isolated from the sulphate partially freed from pseudojervine sulphate by washing with cold water, &c., gave carbon 74·08, hydrogen 9·20, and carbon 74·41, hydrogen 9·44 respectively; the numbers obtained by Will (quoted in § 1) lie between these and those obtained as above stated with pure jervine, from which it may be inferred that Simon's product examined by Will was essentially jervine but containing a small admixture of pseudojervine, which would account also for the low percentage of platinum found in the platinum salt (found 14·55 and 14·33; calculated for $(C_{26}H_{37}NO_3,HCl)_2PtCl_4 = 16·03$).

The water of crystallisation found in these specimens of pure and nearly pure jervine was found to vary considerably; when the crystals were formed from very strong alcohol (90 per cent. spirit) or began to separate whilst the solution was still warm, smaller amounts were found than when the alcohol contained a little more water (70—80 per cent. alcohol) or when the crystals formed in the cold. Thus with five different samples the following numbers were obtained:—

Calculated for $C_{26}H_{37}NO_3$, $2\frac{1}{2}H_2O$.	Calculated for $C_{26}H_{37}NO_3$, H_2O.	Found.
8·12	4·19	8·20
		8·05
		6·84
		5·49
		5·19

Hence, as above stated (§ 2) it is probable that the normal crystals are $C_{26}H_{37}NO_3$, $2H_2O$, but that a little anhydrous base also separated from hot and very strong alcoholic solutions.

The liquors filtered from the jervine sulphate undissolved by water (cold or hot), were precipitated by soda, collected and washed, and again treated with warm dilute sulphuric acid to separate any trace of jervine still present; scarcely appreciable amounts of jervine sulphate were left undissolved; the filtrate contained too little alkaloïdal matter in solution to permit of complete separation of the pseudojervine and rubijervine which it undoubtedly contained, although a partial separation was effected by means of ether; the following numbers were obtained:—

A. Bases precipitated by soda from the filtrate just mentioned and recrystallised from alcohol.

B. Fraction of this mixture left undissolved by agitation with a large bulk of ether.

C. Fraction dissolved by the ether.

	Pseudo-jervine.	Rubi-jervine.	A.	B.	C.
Carbon, in base, dried at 100°	67·31	77·81	69·33	69·25	72·96
Hydrogen „ „	8·32	10·72	8·93	8·95	10·10
Gold in gold salt „	22·90	26·49	—	23·02	—
Melting point (corrected).....	299°	236°	245°	268°	236°

All three of these substances gave with sulphuric acid a colour reaction like that yielded by a mixture of pseudojervine and rubijervine, the alteration of the green tints being more marked with C than with the other two.

From these results it appears that fraction 2 consisted of jervine with a little pseudojervine and somewhat less rubijervine, together with a majority of a different alkaloïd, apparently amorphous and approximating to $C_{28}H_{43}NO_5$, to which we propose to limit the term *veratralbine*.

§ 5. *Examination of Fraction* 4.

The varnish left on evaporation of the ethereal mother-liquor constituting this fraction was powerfully sternutatory in its action when in powder; all attempts to crystallise it from ether, petroleum, benzoline-ether, alcohol, &c., entirely failed, nor could any crystallised salts be obtained; on solution in ether, addition of light petroleum distillate, and spontaneous evaporation, a few centigrams of jervine were obtained, the mother-liquors of which were hopelessly non-crystalline.

The mixture of sulphates left on the filter contained so much pseudojervine that a complete separation of that base by washing with cold water or by regenerating the alkaloïds (by alcohol and sodium carbonate), reconversion into sulphates by dilute sulphuric acid and filtering, appeared to be impracticable; pure jervine sulphate, however, was readily obtained by boiling the mixed sulphates (washed from the majority of the excess of sulphuric acid) with water and filter-pumping hot: by regenerating the base, by means of alcohol and sodium carbonate, jervine was obtained identical with that described above, melting at 239° (corrected) and yielding the following numbers (after drying at 100°) agreeing with $C_{26}H_{37}NO_3$.

0·2195 gram gave 0·6075 CO_2 and 0·182 H_2O.
0·235 „ 0·6465 „ 0·205 „

	Calculated.	Found.	
Carbon	75·91	75·48	75·03
Hydrogen	9·00	9·23	9·69

The colour reaction with sulphuric acid was identical with that yielded by jervine from fraction 3.

Two different specimens of impure jervine isolated from the sulphate partially freed from pseudojervine sulphate by washing with cold water, &c., gave carbon 74·08, hydrogen 9·20, and carbon 74·41, hydrogen 9·44 respectively; the numbers obtained by Will (quoted in § 1) lie between these and those obtained as above stated with pure jervine, from which it may be inferred that Simon's product examined by Will was essentially jervine but containing a small admixture of pseudojervine, which would account also for the low percentage of platinum found in the platinum salt (found 14·55 and 14·33; calculated for $(C_{26}H_{37}NO_3,HCl)_2PtCl_4 = 16·03$).

The water of crystallisation found in these specimens of pure and nearly pure jervine was found to vary considerably; when the crystals were formed from very strong alcohol (90 per cent. spirit) or began to separate whilst the solution was still warm, smaller amounts were found than when the alcohol contained a little more water (70—80 per cent. alcohol) or when the crystals formed in the cold. Thus with five different samples the following numbers were obtained:—

Calculated for $C_{26}H_{37}NO_3$, $2\frac{1}{2}H_2O$.	Calculated for $C_{26}H_{37}NO_3$, H_2O.	Found.
8·12	4·19	8·20
		8·05
		6·84
		5·49
		5·19

Hence, as above stated (§ 2) it is probable that the normal crystals are $C_{26}H_{37}NO_3$, $2H_2O$, but that a little anhydrous base also separated from hot and very strong alcoholic solutions.

The liquors filtered from the jervine sulphate undissolved by water (cold or hot), were precipitated by soda, collected and washed, and again treated with warm dilute sulphuric acid to separate any trace of jervine still present; scarcely appreciable amounts of jervine sulphate were left undissolved; the filtrate contained too little alkaloïdal matter in solution to permit of complete separation of the pseudojervine and rubijervine which it undoubtedly contained, although a partial separation was effected by means of ether; the following numbers were obtained:—

A. Bases precipitated by soda from the filtrate just mentioned and recrystallised from alcohol.

B. Fraction of this mixture left undissolved by agitation with a large bulk of ether.

C. Fraction dissolved by the ether.

	Pseudo-jervine.	Rubi-jervine.	A.	B.	C.
Carbon, in base, dried at 100°	67·31	77·81	69·33	69·25	72·96
Hydrogen „ „	8·32	10·72	8·93	8·95	10·10
Gold in gold salt „	22·90	26·49	—	23·02	—
Melting point (corrected)....	299°	236°	245°	268°	236°

All three of these substances gave with sulphuric acid a colour reaction like that yielded by a mixture of pseudojervine and rubijervine, the alteration of the green tints being more marked with C than with the other two.

From these results it appears that fraction 2 consisted of jervine with a little pseudojervine and somewhat less rubijervine, together with a majority of a different alkaloïd, apparently amorphous and approximating to $C_{28}H_{43}NO_6$, to which we propose to limit the term *veratralbine*.

§ 5. *Examination of Fraction* 4.

The varnish left on evaporation of the ethereal mother-liquor constituting this fraction was powerfully sternutatory in its action when in powder; all attempts to crystallise it from ether, petroleum, benzoline-ether, alcohol, &c., entirely failed, nor could any crystallised salts be obtained; on solution in ether, addition of light petroleum distillate, and spontaneous evaporation, a few centigrams of jervine were obtained, the mother-liquors of which were hopelessly non-crystalline.

With sulphuric acid, the resinous alkaloïd left on evaporation of these final mother-liquors gave exactly the same coloration as the amorphous substance (impure veratralbine) described in § 4; evidently from the mode of separation of the different fractions, the same amorphous base must have been present to a large extent in both fractions, fraction 2 containing that part of it not dissolved by ether on the second treatment of the alkaloïdal matters therewith, and fraction 4 containing that portion of it which was so taken up by the ether.

On analysis the following numbers were obtained approximating to the composition $C_{28}H_{42}NO_5$:—

	Calculated.	Found.
Carbon in base	71·04	70·96
Hydrogen	9·09	9·27
Nitrogen	2·96	2·80
Gold in gold salt	24·14	23·66

Apparently, therefore, this varnish consisted of the non-sternutatory amorphous base, sparingly soluble in ether, above referred to, and provisionally designated veratralbine, with a minute quantity of a sternutatory alkaloïd, probably the veratrine (of Couerbe) described in Part I intermixed therewith: for on cohobation for 20 hours with alcoholic potash a small quantity of veratric acid was formed, whilst the sternutatory action was wholly or almost wholly destroyed. The veratric acid amounted to 2·5 to 3·0 per cent. of the alkaloïdal matter thus treated, indicating an admixture of not more than 10 per cent. of veratrine with 90 per cent. or more of non-saponifiable alkaloïdal matter; it was recognised by its melting point, and the formation of protocatechuic acid on fusion with caustic potash. No trace of cevadic acid was formed during the saponification indicating the absence of cevadine. The admixture of 10 per cent. of veratrine (containing carbon = 64·63, hydrogen 7·71, gold in gold salt 19·10) with an alkaloïd of composition $C_{28}H_{43}NO_5$, would only diminish the percentages of carbon and hydrogen found, and of gold in the gold salt by trifling amounts.

Assuming, as it is highly probable from these results, that the alkaloïd thus present yielding veratric acid on saponification was actually veratrine, and that the sternutatory action of fraction 4 (and consequently of the whole roots examined) was solely due to its presence, it results that the quantity of active alkaloïd present in the roots examined must have been very small: since fraction 4 constituted only about an eighth of the total alkaloïds, the quantity of veratrine could not have exceeded 1·25 per cent. of the total alkaloïds, equal to 0·004 per cent. of the roots examined.

§ 6. *Attempts to obtain Derivatives of Jervine and its Congeners.*

On cohobating jervine for several hours with alcoholic potash, no change whatever is produced in the alkaloïd: no new products of any kind are formed. The base, after cohobation for 24 hours in one experiment, was recovered from the alcoholic liquor by evaporation, washed with alcohol, and converted into gold salt, of which

0·637 gram, dried at 100°, gave 0·1635 Au = 25·66 per cent.
Calculated for $C_{26}H_{37}NO_3$, HCl, $AuCl_3$ = 26·13 „ „

It melted at 233° (corrected); the melting point previously being 236°.

Similar negative results were obtained with pseudojervine as far as the limited amount of the material at our disposal enabled us to judge; as also with the amorphous alkaloïd obtained from fraction 3 (veratralbine): after cohobation with alcoholic potash, the recovered base gave a gold salt containing 22·91 per cent. of gold, the original substance containing 23·18 per cent., whence no alteration in molecular weight had taken place.

An attempt to obtain a benzoylated jervine by fusion with benzoic anhydride led to no definite result; the product when dissolved in alcohol and treated with ether and alkali yielded nothing to the ether capable of being withdrawn by shaking with tartaric acid; nor did it yield anything when boiled direct with tartaric acid, nor could any salt be separated from the excess of benzoic anhydride. Possibly this points to the formation of a benzoylated base, the tartrate of which is insoluble in water, and the free base in ether: we have not made any further attempts in this direction, however, as yet.

§ 7. *Summary of Results.*

(1.) The *Veratrum album* roots examined contained at least five different alkaloïds; of these three are well-defined crystallisable non-sternutatory bases; a fourth is amorphous and non-sternutatory; whilst the fifth is highly sternutatory.

(2.) By the method adopted a rough separation of these alkaloïdal constituents is readily effected, one of the crystallisable alkaloïds (*pseudojervine*) being left behind with but little admixture after the first prolonged treatment with ether; this is, when pure, $C_{29}H_{43}NO_7$; it crystallises anhydrous and is non-sternutatory; it melts at 299°, and forms a crystallisable sulphate and hydrochloride, not of great solubility (especially the latter) in pure water, more soluble in presence of excess of acid and on heating. This base gives a peculiar series of colours with sulphuric acid.

(3.) Of the bases dissolved by ether on the first prolonged treatment, some are much more readily soluble in ether than others, so that on conversion into tartrates, precipitation with soda, and treatment again with much smaller quantities of ether, some are almost completely dissolved out, whilst others are mostly left undissolved. The undissolved bases contain, besides a little pseudojervine, some quantity of *jervine* (of Simon and Will): this is, when pure, $C_{26}H_{37}NO_3$, and is not a dinitrogenous base, as stated by previous observers; it crystallises with $2H_2O$ (somewhat less if the solution be hot or very strongly alcoholic); its sulphate is all but insoluble in water even when hot, and its hydrochloride and nitrate are very insoluble salts. When anhydrous it melts at 237° to 239° (purest specimens) or somewhat lower (not absolutely pure specimens); with sulphuric acid it gives the same tints as pseudojervine.

(4.) In addition, the insoluble portion contains a large quantity of an amorphous non-sternutatory base, apparently indicated by $C_{28}H_{43}NO_5$: to this base we propose to limit the term "veratralbine;" it gives with sulphuric acid a colour reaction quite different from that of jervine and pseudojervine: a trace of the base mentioned in the next paragraph is also present.

(5.) The substances dissolved by ether on the second treatment appear to be free from any appreciable quantity of pseudojervine, but contain jervine, and a third crystallisable non-sternutatory base, *rubijervine*, $C_{26}H_{43}NO_2$; this crystallises anhydrous, melts at close upon the same temperature as jervine (236° purest specimen), forms a hydrochloride and sulphate distinctly more soluble than the jervine or pseudojervine salts, and gives with sulphuric acid an entirely different colour reaction from that yielded by either of these two.

(6.) In addition, the most soluble portion contains a minute amount of a sternutatory alkaloïd yielding veratric acid on saponification (not improbably veratrine); the great majority, however, approximates to $C_{28}H_{43}NO_5$, and is non-saponifiable, and apparently non-sternutatory; this substance gives with sulphuric acid a colour reaction identical with that of the amorphous base referred to in paragraph 4 as *veratralbine*, with which indeed it is obviously essentially identical.

(7.) With the exception of the veratric acid-yielding constituent just referred to, none of the above alkaloïds belong to the saponifiable class.

XLVII.—*The Alkaloïds of the Veratrums.* Part III. *The Alkaloïds of Veratrum Viride.*

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry in St. Mary's Hospital Medical School.

In order to see whether the alkaloïds contained in *Veratrum viride* are in any way related to those isolated as described in Part II from *V. album*, and in particular whether the so-called "viridine" of Bullock is identical or not with jervine, about 18 kilos. (41¾ lbs.) of *V. viride* root (obtained from Messrs. Hopkins and Williams) were percolated with alcohol containing about 130 grams of tartaric acid (about 0·7 per cent. of the weight of the roots), about 15 gallons of alcohol being used, and the percolate from one batch of about 3 or 4 lbs. being used to percolate another batch, and so on in series of four batches, like the lixiviation of black-ash in the alkali manufacture, &c.

The percolate was distilled to a small bulk, treated with water to separate most of the resin, shaken with ether to remove the remainder, and then alkalised with a slight excess of caustic soda and shaken repeatedly with about an equal bulk of ether. Just as with *V. album*, a perceptible amount of alkaloïd remained undissolved even after six treatments with ether; this was collected on a calico filter and examined, when it appeared to be essentially one alkaloïd, apparently the *pseudojervine* described in Part II. The ethereal extract was shaken with tartaric acid solution, and the acid tartrates thus obtained treated with a little caustic soda and fresh ether; the great majority of the precipitate thus obtained dissolved in the ether, yielding a solution from which crystals separated on standing, apparently consisting almost entirely of *jervine*, identical with that from *V. album*; the mother-liquors of these crystals dried up to a varnish resembling the so-called "veratria," similarly obtainable from *V. album*, and like it, possessing all the sternutatory powers of the root; it differed from it however in this respect, that whilst the product from *V. album* yielded veratric acid in small quantity on saponification, and appeared to be a mixture of veratrine (of Couerbe, Part I) with a large excess of veratralbine, an inert base probably indicated by the formula $C_{28}H_{43}NO_5$, the product from *V. viride* yielded on saponification cevadic acid,* and appeared to be almost wholly cevadine (the "veratria" of Merck, and of Schmidt and Köppen). Only a minute quantity of alkaloïd, too, remained undissolved by the ether on this second treatment;

* Doubtless identical with the methyl-crotonic acid of Frankland and Duppa (Part I), and with the tiglic acid of Geuther and others from croton oil.

and this appeared to consist almost entirely of pseudojervine with a little rubijervine; whereas the corresponding fraction obtained with *V. album* roots mainly consisted of the amorphous alkaloïd, $C_{28}H_{43}NO_5$, sparingly soluble in ether (veratralbine).

The total amount of alkaloïdal matter obtained from *V. viride* was only about one-fifth of that from *V. album*, the proportions of the different alkaloïds present being about as follows per kilo. of roots:—

	V. album.	*V. viride.*
Jervine	1·3 gram.	0·2 gram.
Pseudojervine ..	0·4 „	0·15 „
Rubijervine	0·25 „	0·02 „
Veratralbine....	2·2 „	not more than traces.
Veratrine	0·05 „	trace: less than 0·004.
Cevadine	apparently absent.	0·43 gram.
	4·20	0·80

The following numbers and other data were obtained by the further examination of the different fractions isolated as just described.

1*st Fraction.* Base left undissolved by ether after six treatments therewith of the original extract freed from resin and alkalised.

The slightly brown flocculent semicrystalline mass left undissolved by the ether was dissolved in dilute sulphuric acid, which did not leave any insoluble jervine sulphate; the solution was precipitated by caustic soda, filter-pumped, and the residue crystallised from alcohol; snow-white anhydrous crystals thus separated agreeing in every respect with pseudojervine from *V. album*. To purify these further, they were rubbed with a slight excess of dilute hydrochloric acid, and the resulting magma filter-pumped and washed. The filtrate contained besides pseudojervine a minute quantity of rubijervine; at least, on precipitating with soda, filtering, and washing, a small quantity of base was obtained, giving with sulphuric acid a colour reaction precisely like that yielded by a mixture of pseudojervine (giving an emerald-green), and rubijervine (giving a blood-red—crimson-red); the quantity, however, was too small to enable any pure rubijervine to be separated.

The magma of hydrochloride crystals, after draining and filter-pumping, was boiled with alcohol and sodium carbonate: the filtrate deposited snow-white crystals, anhydrous when air-dry, giving the same reaction with sulphuric acid as pseudojervine, and melting at 299° (corrected). The following numbers were obtained by Mr. A. E. Menke on combustion: 0·2575 gram gave 0·6305 CO_2 and 0·1970 H_2O.

		Calculated.	Found.
C_{29}	348	67·31	66·78
H_{43}	43	8·32	8·50
N	14	2·71	—
O_7	112	21·66	—
$C_{29}H_{43}NO_7$ ..	517	100·00	

Like the pseudojervine from *V. album*, the gold salt of this base was not distinctly crystalline.

0·7880 gram of gold salt dried at 100° gave

0·1770 Au ..... = 22·46 per cent.

Calculated for $C_{29}H_{43}NO_7$, HCl, $AuCl_3$ = 22·89 „

The alcoholic mother-liquors of the first crystals obtained before conversion into hydrochloride dried up to a mixture of crystalline pseudojervine and a brownish amorphous alkaloïdal body yielding a dirty red coloration with sulphuric acid ; the quantity of this was too small for separation from the pseudojervine mixed with it ; presumably it was veratralbine, the amorphous base sparingly soluble in ether obtained from *V. album*, and approximating in composition to $C_{28}H_{43}NO_5$.

2nd Fraction. Base left undissolved by ether on treatment of the crude tartrates (obtained by shaking the first ethereal extract with tartaric acid) with soda and ether. So small a quantity of this fraction was obtained, that its quantitative examination was impracticable: it contained no more than traces of amorphous alkaloïd; after crystallisation from alcohol, it wholly dissolved in dilute sulphuric acid, showing the absence of jervine; on treatment with hydrochloric acid, it gave an almost insoluble hydrochloride with a little of a much more soluble salt: the former on boiling with alcohol and sodium carbonate gave a little crystallised pseudojervine melting at 298°, and giving a clear green coloration with sulphuric acid; the latter furnished a crystallised base, giving with sulphuric acid a coloration like that of pseudojervine containing a small quantity of rubijervine; whence doubtless the fraction consisted of these two bases, the latter present only in small quantity.

3rd Fraction. Crystals deposited from the ethereal solution of bases derived from the crude tartrate solution of bases (obtained from the first ethereal extract by shaking with tartaric acid).

These crystals appeared to be jervine free from any appreciable quantity of pseudojervine or rubijervine: they yielded with dilute sulphuric acid a salt almost wholly insoluble in cold water, and almost insoluble in boiling water after freeing from excess of acid by washing. From the filtrates, nothing but jervine was obtained by precipitation

with soda, and only a few centigrams of that. The insoluble sulphate, after boiling with water, was drained, and then boiled with alcohol and sodium carbonate: crystals were obtained on cooling precisely resembling jervine from *V. album*, giving the same colour reaction with sulphuric acid, and melting at 239° (corrected). The following numbers were obtained:—

0·6470 gram of air-dry crystals lost at 100° 0·049 gram = 7·58 per cent.

The specimens from *V. album* lost from 5·19 to 8·20 per cent., the formula, $C_{26}H_{37}NO_3$, $2H_2O$, requiring 8·05 per cent.

0·1415 gram of anhydrous base gave 0·3905 CO_2 and 0·1165 H_2O.
0·1380 „ „ „ 0·3800 „ 0·1140 „

	Calculated.		Found.	
C_{26}	312	75·91	75·26	75·10
H_{37}	37	9·00	9·14	9·18
N.....	14	3·41	—	—
O_3.....	48	11·68	—	—
$C_{26}H_{37}NO_3$ ..	411	100·00		

0·4775 gram of gold salt dried in the air and then over sulphuric acid several days till absolutely constant in weight, lost at 100° 0·0100 gram = 2·10 per cent.

Calculated for $C_{26}H_{37}NO_3$, HCl, $AuCl_3$, H_2O = 2·34 per cent.

0·4675 gram of dried salt gave 0·1200 Au = 25·67 per cent.

Calculated for $C_{26}H_{37}NO_3$, HCl, $AuCl_3$ = 26·13 „

4th Fraction. Amorphous bases most readily soluble in ether (mother-liquors of 3rd fraction), so-called "veratria" or "veratroidia." The amorphous base, $C_{28}H_{43}NO_5$ (veratralbine), sparingly soluble in ether, found to constitute altogether about half of the alkaloïds extracted from *Veratrum album* roots, not having been found to any considerable extent in fraction 2, it would seem probable that the *V. viride* roots examined did not contain any considerable quantity of this substance: whence the alkaloïds most soluble in ether might be anticipated to consist almost wholly of the sternutatory saponifiable alkaloïd found in the *V. album* roots in small quantity. This appears to be the case, with the difference, however, that whilst the sternutatory constituent of *V. album* was apparently veratrine, $C_{37}H_{53}NO_{11}$ (since veratric acid and no appreciable amount of cevadic acid was formed on saponification), the sternutatory constituent of *V. viride* was essentially cevadine, $C_{32}H_{49}NO_9$, only traces of veratric acid being formed on saponification, whilst much cevadic acid was thereby produced.

The following numbers were obtained:—

0·2645 gram gave 0·6310 CO_2 and 0·1985 H_2O.

	Calculated.		Found.
C_{32}	384	64·97	65·06
H_{49}	49	8·29	8·34
N.....	14	2·37	—
O_9	144	24·37	—
$C_{32}H_{49}NO_9$	591	100·00	

0·3760 gram of gold salt dried at 100° gave 0·0805 Au = 21·41 per cent.

Calculated for $C_{32}H_{29}NO_9$, HCl, $AuCl_3$ = 21·08 per cent.

On saponification with alcoholic potash for 24 hours, evaporation and distillation of the residue with dilute sulphuric acid, an acid distillate was obtained containing an acid apparently identical with cevadic acid. The quantity obtained was too small for the isolation of pure crystallised cevadic acid, but it agreed therewith in all its qualitative reactions. 2·380 grams thus yielded acid sufficient to neutralise 5 c.c. of normal alkali solution. The quantity corresponding to 2·380 grams of pure cevadine would be 4·03 c.c. were only cevadic acid formed; but as the experiments described in Part I showed that cevadic acid when thus liberated is partially decomposed forming acetic and propionic acids, an excess of volatile acid would necessarily be formed. The residue left on distilling off the volatile acid was shaken with ether, which extracted 0·041 gram = 1·7 per cent. of substance, chiefly amorphous resinous matter. A trace of veratric acid, however, appeared to be also present, as a minute quantity of a crystalline acid, yielding protocatechuic acid on fusion with caustic potash at 250°, was also left by the ether on evaporation; at most, the amount of veratrine thus probably present could not have amounted to 1 per cent. of the amorphous alkaloïdal mass examined, or less than 0·004 gram of veratrine per kilo. of root. The cevadic acid solution, distilled off and neutralised with sodium carbonate, was evaporated to a small bulk and treated with sulphuric acid and ether, and the ethereal solution allowed to evaporate spontaneously; the oily imperfectly pure cevadic acid thus obtained smelt precisely like that from cevadine; it was readily soluble in water on agitation therewith, and after neutralisation with ammonia, precipitated silver nitrate, ferric chloride, and copper nitrate. After exposure to the air for some hours to remove as far as possible the small quantities of acetic and propionic acid produced by its partial decomposition during formation, it was converted into barium salt by addition of baryta-water and treatment with carbon dioxide to remove

excess; the barium salt solution dried up at 100° to an amorphous salt, of which 0·2375 gram gave ·1645 $BaSO_4$. Ba = 40·72 per cent.

Calculated for $Ba(C_5H_7O_2)_2$ = 40·89 per cent.

All attempts to obtain crystallised cevadine from the amorphous sternutatory mass proved fruitless; but as the total quantity operated on did not amount to many grams, and as this doubtless contained small quantities of other substances, the isolation of cevadine in crystals could hardly have been expected, great difficulty being experienced, as stated in Part I, in obtaining more than a small fraction of the cevadine present in a mixture of alkaloïds in a crystallised state, even when several ounces of mixture are employed. The melting point of the amorphous mixture was found to be about 140° (cevadine melts at 205—206° when pure). With sulphuric acid it gave the same colour reaction as cevadine, utterly different from that of jervine. No crystallisable salts appeared to be formed with mineral acids, the solutions drying up to varnishes.

From the experiments detailed in the preceding three parts of these researches, it results that the Sabadilla seeds examined (Part I) contained the following alkaloïds:—

(1.) Cevadine (veratrine of Merck), $C_{32}H_{49}NO_9$, yielding cevadic, methylcrotonic, or tiglic acid on saponification.

(2.) Veratrine (of Couerbe), $C_{37}H_{53}NO_{11}$, yielding veratric (dimethylprotocatechuic) acid on saponification.

(3.) Cevadilline (in small quantity), $C_{34}H_{53}NO_8$.

The *V. album* roots examined (Part II) contained neither cevadine nor cevadilline, but small quantities of veratrine, to which their sternutatory action was due. In addition, they contained four other bases.

(4.) Jervine (of Simon), $C_{26}H_{37}NO_3$; not saponifiable; crystallisable.

(5.) Pseudojervine, $C_{29}H_{43}NO_7$; not saponifiable; crystallisable.

(6.) Rubijervine (in small quantity), $C_{26}H_{43}NO_2$; not saponifiable; crystallisable.

(7.) Veratralbine, approximately $C_{28}H_{43}NO_5$; not saponifiable; amorphous.

The *V. viride* roots examined (Part III) contained a trace only of veratrine and veratralbine, and only a minute quantity of rubijervine, the alkaloïds present being essentially jervine, pseudojervine, and cevadine, cevadilline being absent. The sternutatory action was here mainly due to cevadine.

XLVIII.—*On a Gold Nugget from South America.*

By Geo. Attwood, F.G.S., Assoc. Inst. C.E., M.Am. Inst. M.E.

In the State of Guayana, Venezuela, South America, a large area of alluvial soil has lately been found to contain gold in paying quantities, and nuggets of 25 ounces in weight have been discovered within three feet of the surface.

The gold deposits are situated in a district called La Pastora, and in about lat. 7° 25′ N. and long. 62° 10′ W. Numerous quartz veins are found in the neighbouring hills, all of which contain more or less gold. The soil is dug up, carried on donkeys to the nearest supply of water, and then washed by the miners in a wooden bowl called a "batèa."

The coarse gold is easily saved; the fine is separated in the form of an amalgam, by the previous addition of a little mercury in the "batèa."

Upon personal examination, I found that fully one-half of the gold nuggets which were produced in this district were covered with a dark-brown substance, resembling a silicate of iron. I also found it customary amongst the miners to beat the nuggets on a blacksmith's anvil (or with two hammers), to clean them before selling to the local merchants.

A nugget which had not been hammered was selected by myself, and, after examination, it afforded the following results:—

Weight	75·00 grains	
„	65·56 „	after fusion with borax.
Loss	9·44 „	in melting = 12·58 per cent.

The nugget was in places covered with earthy matter, which would account for the loss in melting. The fused nugget was now assayed and gave:—

Gold.....	931·4
Silver	068·4
	999·8

A nugget nearly covered with a glazed ferruginous earth was now examined:—

Weight	304·70 grains	before treatment.
„	284·33 „	after treatment with HCl and NaO.

The nugget after being attacked with HCl, the following ingredients were found soluble:—

University of Michigan

Silica.....	0·12	grains
Fe_2O_3.....	8·88	„
CaO	0·15	„
MgO	0·08	„
	9·23	„

The nugget was then treated with NaO, and afterwards with HCl, and the following ingredients were found in solution:—

Silica.....	4·66	grains
Fe_2O_3.....	4·60	„
CaO	0·21	„
MgO	—	
	9·47	

The gangue on the surface of the nugget weighed 20·37 grains, and 18·70 grains were accounted for in the treatment by HCl and NaO, leaving a loss of 1·67 grains. The loss is probably owing to the presence of hydrated oxides of iron.

After the nugget was boiled in HCl, a quantity of fine flour gold, resembling freshly precipitated gold, was found and collected. Having every appearance of being pure, it was carefully tested; but it was found to contain silver similar to the solid portion of the nugget.

A large portion of the nugget's surface, after treatment with HCl and NaO, presented a peculiar appearance, and was found to be partly covered with a coating of fine gold of a dull colour, and which, upon scratching or shaking violently, became detached from the more solid mass.

A portion of the cleaned nugget was then fused with borax.

Weight....	93·14	grains	before fusion.
„	92·50	„	after „
Loss	00·64	„	= 0·68 per cent.

It was then assayed and found to contain:—

Gold.....	945·4
Silver	054·4
	999·8

As a comparative test of the difference in the composition of the gold obtained from the quartz veins and that found in the alluvial soil, a small quantity of gold amalgam was obtained from the Potosi Mining Company's crushing mill, and it contained as follows:—

Mercury....	55·55 per cent.				
Copper	1·79	„	=	4·03 per cent.	in retorted gold.
Silver	3·57	„	=	8·02 „	
Iron	trace	„			
Gold	39·08	„	=	879·40 „	
	99·99				

In the analysis of the amalgam, the fineness of the gold appears less than it is when shipped for market, as the amalgam undergoes a cleaning treatment before melting; also in the fusion the gold is again purified; so that the average assays of a large quantity of gold bars shipped from this district has ranged from 910 to 925 in fineness. The gold obtained from working the quartz veins is always of a baser character than that obtained from the alluvial washings.

In conclusion, *from the above experiments made and recorded on a gold nugget covered with a glazed ferruginous earth, it would appear to me to prove that gold nuggets do gradually increase in size, owing to the accumulation of fresh particles of finely-precipitated gold.*

My laboratory not being in England, Mr. Fred. Claudet has kindly made some of the above experiments for me.

XLIX.—*On Nitrification.* (Part II.)

By Robert Warington.

Before describing the investigations made in the Rothamsted Laboratory since the last communication to the Society (*Trans. Chem. Soc.*, 1878, 44), it may be well to glance at the results recently obtained by other chemists.

It appears that A. Müller (*Land. Versuchs-Stat.*, **16**, 273; *Chem. Soc. J.*, 1873, 1267) was the first to advance the opinion that nitrification is due to the action of a ferment. He observed that pure solutions of ammonium salts or of urea were remarkably stable, while the ammonia of sewage and of certain well-waters rapidly changed into nitric acid. He suggests that the latter solutions probably contain a ferment which effects the transformation.

Two additional papers by Schloesing and Müntz require notice. The first (*Compt. rend.*, **85**, 1018; *Abstracts Chem. Soc.*, 1878, 163) adds another proof to those which they had before advanced, that nitrification is due to an organized ferment. They find that exposure for one hour to a temperature of 100° is sufficient to destroy the power of

nitrification. Soils thus treated were exposed to a current of air, purified by ignition, without nitrification taking place; the addition of a little unheated mould was sufficient to cause nitrification to recommence. The second paper (*Compt. rend.*, **86**, 892; *Abstracts Chem. Soc.*, 1878, 597) describes attempts to produce nitrification by seeding suitable mixtures with various moulds and mycoderms. They employed for this purpose *Penicillium glaucum*, *Aspergillus niger*, *Mucor mucedo* and *racemosus*, and *Mycoderma vini* and *aceti*. In no instance did they obtain nitrification. These low organisms are shown to feed on ammonia and nitric acid, and to convert their nitrogen into organic substance. It is stated that a growth of mould has been long known as injurious to the productiveness of a nitre-bed.

Experiments confirming the ferment theory of nitrification have also been published by F. Storer and others, but without any new light being thrown on the subject.

In my previous communication it was shown that weak solutions of ammonium chloride, containing small quantities of tartrate and phosphate of potassium, with an excess of calcium carbonate, could be readily nitrified by seeding them with a few drops of another solution which had already undergone nitrification. Nitrification being thus producible at will, an excellent opportunity seemed to be presented of studying the conditions under which it took place. Experiments in solutions appeared also to afford a simple and accurate mode of investigation: for though oxidation is probably far slower in a solution than in a porous soil, the solution has the great advantage of being readily made of any composition desired, and the changes which take place in it can be easily ascertained from time to time.

The primary objects of the present experiments were to ascertain the influence of light and temperature, and of variations in the composition and concentration of the solutions, on the process of nitrification. The attempt was also made to study the rate at which nitrification progresses, and the relation of the nitric acid produced to the ammonia consumed. Other points of interest have also been dealt with. The whole work is as yet confessedly imperfect. It appeared, however, better to publish the results already obtained than to wait till a complete answer could be given to these questions, especially as many of the results are now considerably more than a year old.

It must be borne in mind, while following the ensuing account, that several series of experiments were simultaneously in progress; the experience gained in one series could not therefore always be made use of in another series. In giving the history of the solutions, only the more important dates are mentioned, some intermediate qualitative testings being omitted. A summary of the conclusions arrived at will be given at the end of the paper.

First Series. Bottles A.

This series consisted of four bottles, the contents and behaviour of which have been described down to December 19, 1877, in the first report of these experiments.

The bottle AL2, which had been twice seeded with soil, and freely exposed to light, remained unnitrified after more than eleven months, when the experiment was concluded. A green growth had formed in this bottle. It will be recollected that the corresponding bottle kept in darkness (AD2) completely nitrified, and that from this bottle the two remaining bottles, AL and AD, were seeded.

Bottle AD, kept in darkness, had commenced nitrification when examined 22 days after seeding, and nitrification was completed by December 19. The corresponding bottle, placed in the window (AL), contained no nitric acid 49 days after seeding: no green growth was visible. On December 21 this bottle was placed in the dark cupboard and seeded afresh, by adding 1 c.c. from AD. Examined on February 21, the ammonia originally present was found to be completely nitrified.

Solution AD is the only one in this series in which the course of nitrification was regularly followed. The results obtained from the date of seeding to that of complete nitrification were as under.

Date.	Interval.	Nitrogen as nitric acid.	Nitrogen daily oxidised.
1877.		per million.	per million.
October 15	—	—	—
November 6	22 days.	0·7	—
„ 19	13 „	2·0	0·10
December 3	14 „	11·9	0·71
„ 19	16 „	20·1	0·51
Mean rate of action during 43 days			0·45

Seeding was thus followed by a period of inaction, which we may perhaps style the period of incubation. This is succeeded by a period of action, in which the activity increases up to a certain stage, and then diminishes again as the nitrification approaches completion. This mode of procedure will be found to hold good for all the subsequent examples of nitrification which have been fully studied.

In these first experiments the nitrifying germ was obtained from the soil of a fairy ring; no further recourse has been had to this original source of the ferment, all subsequent solutions being seeded from bottles AD or AL, or from some of their descendants.

In this series of experiments the effect of light is absolute in preventing nitrification.

Second Series. Bottles B.

The primary idea with which this series commenced was to ascertain whether the mycelium from a fairy ring would act as a nitrifying ferment. Eight wide-mouthed stoppered bottles of pale green glass were filled to the shoulder with a solution containing chloride of ammonium equal to 20·6 milligrams of nitrogen per litre, with a little sulphate of potassium; a small quantity of dry precipitated phosphate of calcium was also added to each bottle. Four of the bottles then received acid tartrate of potassium equal to 200 milligrams per litre. Four were also seeded with a fragment of mycelium, weighing in each case three- or four-tenths of a milligram. The mycelium was part of a stout sheet lying among the grass roots upon the surface of the turf. Heated on platinum foil it blackened, and evolved an odour of burning horn. The bottles now contained as follows:—

BD and BL,	general solution.	
BD2 and BL2,	,,	and tartrate.
BD3 and BL3,	,,	and mycelium.
BD4 and BL4,	,,	tartrate and mycelium.

The BL's were placed on October 16, 1877, in an east window, and the BD's in a dark cupboard beneath the same window.

On November 5 a growth of mould was noticed in each of the bottles containing tartrate.

On November 9 some precipitated carbonate of calcium was added to bottles BD2 and BL2, and on November 19 the same was added to BD3 and BL3.

The solutions were tested from time to time up to December 19, but no nitric acid was found; all the bottles were then seeded with 1 c.c. of the nitrified solution AD; the solution was shaken before the portions used for seed were taken.

On January 10, 1878, nitrification was found to have commenced in BD2 and BD4, most progress having taken place in the first named.

On February 21 the nitrification of BD2 was found to be completed, all ammonia having disappeared. The solution, when examined by the indigo method, yielded 18·7 parts of nitrogen as nitrates per million.

On March 20 nitrification having made very little progress in BD4, some precipitated carbonate of calcium was added to the solution; the solution at this date contained a considerable amount of nitrous acid.

On April 24 the nitrification of BD4 was found completed; neither ammonia nor nitrous acid was present. The nitric acid found equalled 19·1 parts of nitrogen per million.

Solution BD3 contained on February 21 no nitric acid, but when examined on June 25 it was found to be completely nitrified. BD has remained unnitrified during 16 months.

The bottles placed in the window were neglected, it being too hastily assumed that they would not nitrify. On June 25, it was found that BL2 had nearly finished nitrification; a trace of ammonia and a little nitrous acid were present. A small green growth covered the surface of the glass. In BL3 nitrification had begun; but here both ammonia and nitrous acid were in considerable quantity. The solutions were not again examined for ten months, at the end of which time no ammonia could be detected in BL3, but a considerable amount of nitrous acid was present. BL and BL4 have remained quite unnitrified.

The conclusions to be drawn from these experiments are important. In the first place, the mould which developes in a solution containing tartrates is shown to be incapable of effecting nitrification. In four of the bottles this growth of mould appeared; two of the bottles were kept in the dark 44 days, and one of these contained an excess of carbonate of calcium during the last 40 days, but no trace of nitric acid was produced. The ineffectiveness of the mycelium from the fairy-ring is less certainly proved, for in no case was it used in conjunction with carbonate of calcium. One bottle, however, was supplied with tartrate of potassium, and kept in darkness 64 days, and in this case a little nitric acid should have been found if the mycelium had the power of acting as a nitrifying ferment.

Turning to the results obtained after seeding with a ferment of known efficacy, we see that in no case is nitrification completed except where carbonate of calcium has been present. The bottle (BD) containing chloride of ammonium solution, supplied with phosphate of calcium and phosphate of potassium, contained only a trace of nitric acid after 16 months, though kept in darkness, and seeded with an active nitrifying ferment. When, in addition to these ingredients a little acid tartrate of potassium was supplied, a small amount of nitrification took place. Bottles BD2 and BD4 both contained tartrate of potassium, but only the first named contained carbonate of calcium when the seed was added. The ammonia in this bottle was found completely nitrified 64 days after seeding, while in BD4 but little nitrification had taken place in 84 days, and no progress had apparently been made during the last 20 days. When carbonate of calcium was added to this bottle nitrification became speedy, and was soon accomplished. The small amount of nitrification which took place before the addition of the carbonate of calcium was probably due to the decomposition of the organic potassium salt, which would produce a little carbonate of potassium serving the same function as the calcium

carbonate. I have elsewhere shown (*Chem. Soc. J.*, 1875, 968) that the growth of mould in a solution of acid tartrate of potassium results in a feebly alkaline solution.

Another point which comes out in a striking manner is the very small amount of organic carbon which is requisite for nitrification. Bottles BD3 and BL3 contained only the carbonaceous matter supplied by the minute quantity of mycelium, and by the small amount of seed solution, containing tartrates, introduced, with of course the minute quantity supplied by the distilled water and atmosphere. This quantity proves, however, sufficient to effect nitrification, though a very long period is occupied in its completion. Bottle BD3 showed no nitric acid 64 days after seeding; tested again in summer time, 124 days later, nitrification was found to be complete. At this last date BL 3 still contained much ammonia, but 10 months afterwards the ammonia had disappeared, though much nitrous acid was still present.

The influence of light in this series was not an absolute prevention of nitrification; the contents of two bottles nitrified, though exposed to light. Unfortunately the date when nitrification commenced is unknown, but in the case of BL3 it is evident that nitrification proceeded much more slowly than in the corresponding bottle kept in darkness.

Third Series. Bottles C.

This series consisted only of two bottles; it was designed to show more plainly the importance of a salifiable base for nitrification. Tartrates had generally been employed in the preparation of solutions for nitrification; they possess the great advantage of being without influence on the determination of nitric acid with indigo. Such salts could not, however, be employed without the introduction of some salifiable base, as the consumption of the tartaric acid by an organism must result in the formation of an alkaline carbonate. In the present case cane-sugar was used in place of a tartrate. The solution contained in 1 litre chloride of ammonium equal to 20·5 milligrams of nitrogen, 50 milligrams of cane-sugar, and a very little phosphate of potassium, gypsum, and sulphate of magnesium. Bottles C and C2 were partly filled with this solution; to the latter bottle some precipitated carbonate of calcium was added. Both bottles were seeded on December 21, 1877, with 1 c.c. from AD, and were then placed in a dark cupboard.

The action was very slow in commencing. On January 10, 1878, no nitric acid was found in either bottle. On February 21, nitrification was found to have commenced in C2, but no change was observed in C. On March 23 the nitrification in C2 was almost completed,

very little ammonia was present, and no nitrous acid. At the same date C contained a trace of nitrous acid. On March 27 the nitrification of C2 was found to be completed.

The experiment in bottle C was allowed to go on till April 18, at which time a small quantity of nitrous acid was present, but no significant amount of nitrification had taken place. Precipitated carbonate of calcium was now added to the contents of the bottle. On May 3 nitrification had considerably advanced, and on May 25 no ammonia was present.

A marked difference was observed between C2 and C respecting the production of nitrous acid. C2, which had carbonate of calcium from the first, seems to have produced no nitrous acid; while in the case of C the nitrification which occurred after the late addition of carbonate of calcium was wholly nitrous. On May 16 the nitrogen present as nitrous acid amounted to 18·1 per million. After nitrification was completed the nitrous acid gradually diminished in quantity, and on June 17 none was found. A similar, but less marked production of nitrous acid, was observed in the case of BD4 in the preceding series, in which, as in the present instance, nitrification was commenced in the absence of calcium carbonate.

In the case of C2 the course of nitrification was as follows:—

Date.	Interval.	Nitrogen as nitric acid.	Nitrogen daily oxidised.
1877.		per million.	per million.
December 21.....	—	—	—
1878.	—	—	—
February 21.....	62 days.	1·1	—
March 12.....	19 „	13·1	0·63
„ 27.....	15 „	18·7	0·37
Mean rate of action during 34 days			0·52

The rate of nitrification is here very similar to that shown by solution AD.

The fact that the presence of a salifiable base is necessary for nitrification, which the results of both this and the preceding series of experiments illustrate, is one of great practical importance. It helps to explain why peat-waters, and soft waters generally, are usually free from nitrates. It throws new light on the well-known value of lime as a dressing for many soils, and especially on its importance in reclaiming peat-land, for which purpose lime is absolutely essential. When we understand that the nitrogenous humic matter of soils, which is apparently useless as plant food, can only be oxidised into

nitrates in the presence of a salifiable base, the function of chalk and lime in agriculture becomes better understood. Peat soils entirely consist of such nitrogenous humic matter, and till lime is applied it is probable that nitrification never takes place.

Fourth Series. Bottles D—G.

In this, the most extensive series among the present experiments, the design was—1. To ascertain the influence of temperature, by conducting the nitrification in baths the temperature of which was invariable. 2. To ascertain the effect of concentration of the solution, by nitrifying solutions of graduated strengths. 3. To determine the minimum proportion of organic carbon necessary for the nitrification of ammonia. 4. To study the rate of nitrification at fixed temperatures by repeated quantitative analyses of the solutions.

The composition of the solutions employed will be gathered from the following table. The figures represent milligrams per litre; or, in other words, parts per million:—

Name of bottle.	Chloride of ammonium.	Rochelle salt.	Phosphate of potassium.	Sulphate of magnesium.
D	80	150	20	5
D2	80	150	20	5
D3	640	1200	160	10
D4	640	1200	160	10
E	80	150	20	5
E2	640	300	40	5
E3	640	600	80	5
E4	640	1200	160	10
F	80	150	20	5
F2	160	300	40	5
F3	320	600	80	5
F4	640	1200	160	10
G	80	150	20	5
G2	640	1200	160	10

It was intended that the D solutions should be kept at the temperature of the air; the E solutions at 20°; the F solutions at 30°; the G solutions at 40°. Two of the solutions employed, namely, the weakest and strongest, formed part of each of the sub-series; the behaviour of the same solution at different temperatures could thus be studied. In sub-series E there was a graduated proportion of organic carbon (tar-

taric acid) to ammonia. In sub-series F there was a graduation in the concentration of the solutions employed.

The solutions were placed in wide-mouthed pint bottles, filled to the shoulder. The bottles were all supplied with precipitated carbonate of calcium, and seeded with 1 c.c. from bottle AD on March 1, 1878. Those bottles which were to be kept at fixed temperatures were then placed in water-baths, maintained at a nearly uniform heat by means of a gas regulator immersed in the water. The regulator first employed was the ordinary one acting by the expansion of air; this was afterwards changed for Page's mercurial regulator, which proved far more safe and accurate. The bottles left at the temperature of the air were placed in a cool cupboard, the temperature of which was daily ascertained. All the bottles were protected from light.

The solutions were thoughtlessly seeded on a day when some hay was being moved in the laboratory. By March 5 all the stronger solutions in the bath had become more or less turbid from the growth of bacteria, the greatest turbidity being in E3 and F3. On March 12 the turbidity was found to have increased, and had extended to all the bottles. The turbidity was greater in proportion to the strength of the solutions. Thus in sub-series E and F the turbidity followed the order of the numbers, being greatest in E4 and F4. These two solutions, together with G2, had now a considerable film on the surface, and smelt like a rotten turnip.

On March 20 samples from F and E4 were sent to Professor Dyer, who kindly submitted them to a microscopical examination. E4 was reported as swarming with bacteria; F as containing some of these organisms. On April 1 the turbidity of the bottles in the baths had generally diminished, and continued to do so from this date. Bottles D3 and D4 were now the most turbid in the series, and held this position to the end of the experiment. Bottle G was remarkably clear.

In order to renew the air in the bottles the stoppers were removed for a few moments two or three times a week; the bottles were also necessarily opened from time to time when taking samples for examination; the possible entrance of germs was thus unavoidable.

Nitrification was not detected in any solution on March 5.

On March 12 nitrification was found to have made distinct progress in F, standing in the bath at 30°; no other solution showed change.

On March 18 only a trace of ammonia remained in F. Nitrification was found to have commenced in F2 and F3; also in E and E2, standing in the bath at 20°.

On March 20 the solution in bottle F4 showed a distinct amount of nitrous acid when acidified with sulphuric acid, and tested with a drop of starch solution containing iodide of potassium. Bottle E3 also contained a little nitrous acid.

On March 23 very little ammonia was found in E, and on March 25 nitrification was complete. Nitrification had now made rapid strides in E2, F3, F2, E3, and F4, the progress being apparently in the order named.

On March 27 nitrous acid was distinctly found in E4. All the solutions in the baths kept at 20° and 30° had now commenced nitrification, and the two weakest solutions had completely nitrified; no start had, however, been made in the bottles at 40°, or in those at the temperature of the air.

In examining these solutions with indigo a great disappointment was experienced. It was intended to study the varying intensity of nitrification from the beginning to the end of the process by means of frequent quantitative determinations with indigo. On examining solution F, after all ammonia had disappeared, a novel and very unsatisfactory reaction was obtained. On pouring the oil of vitriol into the mixture of solution and indigo, the action on the indigo was immediate, instead of occupying, as usual, an appreciable time. There was also no sharpness in the result, quantities of indigo distinctly different giving nearly the same final tint. The maximum quantity of indigo used was also far below that required if the ammonia which had disappeared had been converted into nitric acid. The explanation of these reactions was soon found; nitrous acid instead of nitric had been produced, and was the cause of these abnormal results. As the indigo method clearly failed in the presence of nitrous acid, the study of the course of nitrification was greatly interfered with.

Attention was now turned to the determination of nitrous acid by solution of permanganate of potassium. It was found that the solutions of tartrates, &c., employed for nitrification did not decolorise permanganate, even when acidified with sulphuric acid. Solutions which had nitrified, but which contained no nitrites, had also no effect on permanganate. It seemed, therefore, feasible to determine the quantity of nitrous acid formed by the use of this reagent. The solutions of permanganate employed were standardised from time to time with crystallised sulphate of iron and ammonium; 56 parts of this salt correspond to 1 part of nitrogen as nitrous acid. 1 c.c. of the permanganate used generally equalled about ·00015 gram of nitrogen. The mode of determining was to place 10 c.c. of the solution in a small beaker, add some permanganate, then a few drops of dilute sulphuric acid, and then, as the colour disappeared, a further quantity of permanganate, till the tint produced by one drop was not wholly discharged in five minutes.

On April 2 solution F2 was found completely nitrified; abundance of nitrous acid was present. At this date G and G2 were seeded afresh; the first with 1 c.c. from Bottle F; the second with 1 c.c. from F4.

On April 6 a sad accident happened to the F bath (30°); an india-rubber of the gas regulator burst, and the temperature was found as high as 55°. Bottles F and F2 had been taken out of the bath when nitrification was completed, and escaped this disaster. The temperature series being thus broken, the E bath was raised from 20° to 30°, the latter temperature being thought more favourable to nitrification.

On April 8 signs of nitrification appeared for the first time in D and D2, the weak solutions which had been placed in the cool cupboard.

On April 24, no nitrification having appeared during 54 days in bottles G and G2 kept at 40°, the temperature of the bath was lowered to 30°.

On April 30 nitrification was found to have made considerable progress in bottles D and D2; and in striking contrast to the bottles in the baths, the nitrification which occurred was purely nitric, especially in the case of D, which gave a trace of nitrous acid only at the first starting of the oxidation. Solution D now contained, by experiment with indigo, 10·1 of nitrogen per million in the form of nitric acid, and solution D2, 6·4 parts. In all previous experiments on the effect of light the solutions had been exposed when freshly seeded, and before nitrification had become active; it seemed possible that a solution rapidly nitrifying might be better able to withstand the prejudicial influence of light than one in which the ferment was small in quantity, and had not yet entered on its active phase of existence. At this date bottle D, henceforth called DL, was placed in a south window, and at once exposed to bright sunshine; a similar bottle filled with water, and provided with a maximum thermometer, was placed beside it to mark the highest temperature to which it was exposed. Bottle D2 remained in the cool cupboard.

On May 15 nitrification was completed in D2; no nitrous acid was present. Analysed by indigo it gave 20·0 parts of nitrogen per million existing as nitric acid. DL when examined with indigo was found to have made no advance; it decolorised the same amount of indigo as on April 30th. A trace of nitrous acid was present. The maximum thermometer showed that the temperature had once reached 35°; this temperature was attained on May 12. The prejudicial effect of light is strikingly shown by this experiment.

Bottle DL was now placed in a dark bath at 30°, with a view to discover whether the nitrifying germs had been killed by exposure to light. On June 3 nitrification was found to be complete; a large amount of nitrous acid was present. On June 17 a determination with permanganate showed the quantity of nitrous acid to equal 9·0 of nitrogen per million; the nitrification in the bath had thus been wholly nitrous.

The bottle was kept in the bath, and on July 8 the nitrous acid was found to have disappeared.

On May 18, nitrification was first observed in solutions D3 and D4, the strong solutions in the cool cupboard; nitrous acid was present in each case. At the same date G and G2 were seeded for the third time, 1 c.c. from bottle AL being added to each. The ferment had apparently been killed in these solutions by long exposure to the temperature of 40°; this is at least the natural conclusion from the fact that they had remained 24 days at the favourable temperature of 30° without nitrification taking place.

On May 25 nitrification was found to be complete in the case of E3 and E4, nitrous acid had also disappeared. In E2 ammonia was still abundant.

On May 30 nitrification had commenced both in G and G2; most progress had been made in the former.

On June 7 solution E2 was found to be completely nitrified; nitrous acid as well as ammonia had disappeared.

On June 17 nitrification was completed in G; only a trace of nitrous acid was present.

On July 30 solution G2 had completely nitrified; nitrous acid was absent.

On October 4 solution D3 was found to be completely nitrified; nitrous acid had disappeared. In the duplicate bottle D4, a large quantity of nitrous acid and a little ammonia were present.

On October 15 no ammonia was found in D4; nitrous acid was still large.

The history of all the seeded bottles has now been sketched; two bottles which remained unseeded require a short notice. The solutions in question were the duplicates of F2 and E3. They were placed in new bottles, which had been simply rinsed with distilled water, but not chemically cleaned and heated in the water-bath, as was the case with the other bottles used in this series. The solutions also were not heated before being placed in the bottles. The bottles were preserved in a dark cupboard.

On March 9 some carbonate of calcium was added to F2′, but none to E3′.

On May 25 no ammonia was found in F2′, but a considerable amount of nitrous acid was present. Nitrification was thus completed in 85 days, without artificial seeding.

On May 6, 1879, bottle E3′ was examined. It contained nitric acid equal to 30·8 of nitrogen per million; no nitrous acid was present. Rather less than $\frac{1}{5}$th of the ammonia present had thus nitrified in 14 months without artificial seeding, and in the absence of lime, tartrate of potassium was however present.

We have now completed the diary of these experiments, and must next attempt to summarise their teaching.

One of the objects with which the experiments were planned was to ascertain how strong a solution of chloride of ammonium could be nitrified; this object was not attained, as the strongest solution used (640 milligrams per litre) was completely nitrified.

It has been made tolerably evident that bacteria are incapable of producing nitrification. Bacteria occurred in bottle G, and swarmed in G2, yet these two bottles were maintained 54 days at 40°, and 24 days at 30°, without nitrification commencing. Bacteria were also extremely abundant in bottles D3 and D4; yet these solutions remained 78 days at a mean temperature of 10° before nitrification commenced. These experiments at least prove that bacteria may flourish in ammoniacal solutions of favourable composition without producing nitrification.

Some light has also been thrown on the limits of temperature at which nitrification is possible. It has been shown that in the case of solutions the temperature must be below 40°; but the maximum temperature at which nitrification will take place has not been ascertained. The record of temperature also affords evidence that nitrification will proceed with some briskness at 10°, and probably at still lower temperatures.

The effect of different temperatures on the duration of the two periods of incubation and of action, in the case of solutions varying both in concentration and composition, is shown by the following tables. The periods observed in some of the earlier experiments are given together with the more recent results.

Periods of Incubation.

Approximate strength of solutions. Milligrams NH_4Cl per litre.	Temperature 7°–10°.		Temperature 20°.		Temperature 30°.	
	Bottle.	Days.	Bottle.	Days.	Bottle.	Days.
80	AD	22*	E	17	F	11*
	D	31	—	—	G	12*
	D2	38	—	—	—	—
160	—	—	—	—	F2	17
320	—	—	—	—	F3	17*
640	D3	78	E 2	17*	F4	19
	D4	78	E 3	19	—	—
	—	—	E 4	26	—	—

The periods marked with an asterisk are known to be somewhat

longer than the truth, nitrification having made some little progress before its commencement was observed.

With solutions of the same strength and composition—as the weak solutions D, D2, E, F, and G, or the strong solutions D3, D4, E4, and F4,—the period of incubation is considerably shortened by a rise in temperature. The extreme periods observed with the weak solutions are 38 days in the case of D2 (mean temperature 7°·6), and about 10 days in the case of F (temperature 30°). With the strong solutions the extremes are 78 days in the case of D3 and D4 (mean temperature 10°), and 19 days in the case of F4 (temperature 30°). The period of incubation is distinctly shorter at 30° than at 20°, as we see by comparing E with F, and E4 with F4.

As the solutions become stronger the period of incubation evidently tends to lengthen.

Periods of Action.

Approximate strength of solutions. Milligrams NH_4Cl per litre.	Temperature 10°–16°.		Temperature 20°.		Temperature 30°.	
	Bottle.	Days.	Bottle.	Days.	Bottle.	Days.
80.....	AD	43	E	7	F	7†
	BD2	42	—	—	—	—
	C	37	—	—	—	—
	C2	34	—	—	—	—
	D2	37	—	—	—	—
160.....	—	—	—	—	F2	15*
640.....	D3	139	—	—	G2	61
	D4	147	—	—	E2	81
	—	—	—	—	E3	66
	—	—	—	—	E4	59

Some of these periods are probably somewhat longer than the truth, nitrification having ceased before the fact was ascertained. On the other hand the period marked with a dagger is too short, as a part of the time accredited to incubation was really taken up by action.

The period of action becomes much shorter as the temperature rises; but it is not clear that in this respect 30° gives a better result than 20°, the only comparative experiment being rather in favour of the lower temperature. The extreme periods in the case of weak solutions of the same composition were 37 days in the case of D2 (mean temperature 12°·0), and 7 days in the case of E (temperature 20°). With the strong solutions we have 147 days for D4 (mean temperature 16°·2), and 61 days for G2 (temperature 30°).

The period of action in solutions of different strengths maintained

at the same temperature varies apparently pretty directly with their degree of concentration. Thus nitrification in F occupied about 8 days; in F2, a solution of twice the strength, it occupies 15 days, or perhaps rather less; while in G2 and E4, eight times the strength of F, the period is 61 and 59 days. It must be recollected that in the case of E2, E3, and E4, the first 19 days of nitrification took place at 20°, and not at 30°.

The series E2, E3, and E4 comprises the solutions containing an increasing proportion of Rochelle salt and phosphate of potassium. The solution containing the smallest proportion of these salts (E2) is the first to commence nitrification, while that containing the largest proportion (E4) is the last to make a start; the presence of saline matter thus apparently hinders the commencement of nitrification. The period of action follows, however, a reverse order, being shortest in E4 (59 days), where the supply of organic carbon and phosphates was largest, and longest in E2 (81 days), where these necessary constituents were present in one-fourth the quantity.

The proportion of organic carbon to nitrogen in E2 is approximately as 3 : 10; this is evidently sufficient for the requirements of nitrification. The minimum proportion of carbon necessary for nitrification has not yet been determined. The proportion present in the case of experiments BD3 and BL3 was probably far smaller than in E2.

We next turn to the evidence afforded by these experiments as to the rate at which nitrification proceeds in different stages of its progress, and the different character it assumes under different circumstances. To do this it will be necessary to tabulate the results of the periodical examinations of the solutions most thoroughly studied.

Bottle.	Date.	Interval.	Temperature.	Nitrogen per million			
				As ammonia.	As nitrous acid.	As nitric acid.	Daily oxidised.
	1878.						
D2 ..	March 1	—	—	20·8	—	—	—
	April 8	38 days	6°·9	abundant	trace	trace	—
	„ 30	22 „	10°·0	abundant	none	6·4	0·30
	May 15	15 „	13°·2	none	none	20·0	0·91

Mean rate of action during 37 days at 11°·3 ..... 0·54

Bottle.	Date.	Interval.	Temperature.	Nitrogen per million			
				As ammonia.	As nitrous acid.	As nitric acid.	Daily oxidised.
D3 ..	March 1	—	—	166·9	—	—	—
	May 18	78 days	9°·3	abundant	considerable	—	—
	June 17	30 „	13°·0	„	24·5	—	0·82
	July 8	21 „	17°·5	„	50·8	—	1·25
	„ 29	21 „	17°·8	„	76·8	—	1·24
	Sept. 5	38 „	17°·0	„	93·4	—	0·44
	„ 19	14 „	15°·5	„	5·2	—	—
	Oct. 4	15 „	13°·0	none	none	143·7	—
	Mean rate of action during 139 days at 15°·8						1·03
D4 ..	March 1	—		166·9	—	—	—
	May 18	78 days	9°·3	abundant	trace	—	—
	June 17	30 „	13°·0	„	16·2	—	0·54
	July 8	21 „	17°·5	„	43·4	—	1·30
	„ 29	21 „	17°·8	„	73·4	—	1·43
	Sept. 5	38 „	17°·0	„	108·3	—	0·92
	„ 19	14 „	15°·5	„	120·6	—	0·88
	Oct. 4	15 „	13°·0	distinct	116·2	—	—
	„ 12	8 „	15°·3	none	100·4	—	—
	„ 15	3 „	9°·1	„	79·4	—	—
	Nov. 4	20 „		„	none	158·0	—
	Mean rate of action during 147 days at 15°·7						1·07

We have here three examples of ammoniacal solutions nitrified at the temperature of the air. The first is a weak solution; the last two are duplicates of eight times greater strength.

In the case of the weak solution the character of the nitrification is purely nitric, no nitrous acid being formed except a minute quantity at the commencement. The same result was obtained in all the earlier experiments with weak solutions of normal composition nitrified in the dark at low temperatures. In the case of bottle C, however, a weak solution from which carbonate of calcium was long withheld, it will be recollected that the nitrification was purely nitrous.

With the stronger solutions the character of the nitrification is very different. Large quantities of nitrous acid are at first produced, and the nitrification is probably for some time wholly nitrous, though this cannot be proved, as no quantitative determinations of the total nitrous and nitric acids were made.

The manner in which nitrification concludes is not always the same. With D3 the nitrous acid probably disappeared before all the ammonia

had been consumed, as the latter was still considerable in quantity on September 27. If this be so, the last stage of the nitrification was purely nitric in character. With D4, on the other hand, the nitrous acid survives the ammonia, and gradually changes into nitric. The period of action in all such cases has been reckoned from the disappearance of the ammonia.

The mean rate of oxidation is about twice as great in the strong solutions as in the weak, the former having, however, the more favourable temperature. A gradual increase in the rapidity of the action up to a certain point, followed by a decline towards the end, is not shown in the case of D2, but appears distinctly (if we may trust the determinations of nitrous acid as expressing the whole action) in solutions D3 and D4.

We turn now to the results obtained at higher temperatures.

There is only one experiment (E) in which nitrification was entirely conducted at the temperature of 20°. In this case the character of the action was decidedly nitrous, but no quantitative determination of nitrous acid was made. The nitrous acid continued present for one or two weeks after all ammonia had disappeared. The temperature during this time was maintained at 20°.

In the similar solution (F) nitrified at 30°, the character of the reaction was purely nitrous. The solution when nitrified was placed in a cool cupboard. After 36 days it was found to contain 18·0 parts of nitrogen per million in the form of nitrous acid, the amount originally present as ammonia being 20·9 parts. The bottle was then placed again in the bath at 30°. After nine days the nitrogen as nitrous acid had fallen to 10·6 per million. Examined two weeks later the nitrous acid had entirely disappeared.

In solution F2 the reaction was again purely nitrous. The solution when nitrified was placed in a cool cupboard. After 22 days the nitrogen as nitrous acid amounted to 39·9 per million, the amount originally present as ammonia being 41·7 per million. The bottle was then returned to the bath at 30°, but after 36 days still contained 35·6 of nitrogen as nitrous acid. Examined about two weeks later the nitrous acid had disappeared.

Experiments F3 and F4 were spoilt, as already mentioned, by the accident to the bath containing them. Determinations of nitrous acid were made in both on their removal from the bath. The rate of progress up to this date is therefore known.

In G2 one determination of nitrous acid was made. In this solution the nitrous acid disappeared before the ammonia.

The mean daily rate of oxidation in these partially studied solutions was as follows:—

Bottle.	Temperature.	Interval.	Nitrogen per million daily oxidised.
E	20°	Whole period of action	2·89
F	30°	,, ,,	2·50
F2	30°	,, ,,	2·66
F3	30°	First 20 days	2·96
F4	30°	First 17 days	3·71
G2	30°	First 18 days	3·79

As the numerical results obtained in the case of solutions E2, E3, and E4 are somewhat more complete, it will be better to give them before discussing the subject.

Bottle.	Date.	Interval.	Temperature.	Nitrogen per million			
				As ammonia.	As nitrous acid.	As nitric acid.	Daily oxidised.
	1878.						
E2 ..	March 1	—	—	166·9	—	—	—
	,, 18	17 days	20°	abundant.	considerable	—	—
	April 6	19 ,,	,,	,,	abundant	—	—
	,, 9	3 ,,	30°	,,	80·6	—	3·66
	,, 17	8 ,,	,,	,,	99·4	—	2·35
	May 3	16 ,,	,,	,,	122·5	—	1·44
	,, 17	14 ,,	,,	,,	135·3	—	0·91
	,, 30	13 ,,	,,	distinct	none	—	—
	June 7	8 ,,	,,	none	,,	182·5	—
	Mean rate of action during 81 days						2·06*
E3 ..	March 1	—	—	166·9	—	—	—
	,, 20	19 days	20°	abundant	distinct	—	—
	April 6	17 ,,	,,	,,	abundant	—	—
	,, 9	3 ,,	30°	,,	63·1	—	3·16
	,, 17	8 ,,	,,	,,	87·4	—	3·04
	May 3	16 ,,	,,	,,	58·6	—	—
	,, 17	14 ,,	,,	considerable	none	—	—
	,, 25	8 ,,	,,	none	,,	170·7	—
	Mean rate of action during 66 days.....						2·53*
E4 ..	March 1	—	—	166·9	—	—	—
	,, 27	26 days	20°	abundant	distinct	—	—
	April 6	10 ,,	,,	,,	abundant	—	—
	,, 9	3 ,,	30°	,,	48·4	—	3·72
	,, 17	8 ,,	,,	,,	84·7	—	4·54
	May 3	16 ,,	,,	,,	137·0	—	3·27
	,, 17	14 ,,	,,	considerable	132·1	—	—
	,, 25	8 ,,	,,	none	none	169·5	—
	Mean rate of action during 59 days						2·83*

In all these experiments made at high temperatures, whether with weak or strong solutions, the character of the action is decidedly nitrous. In F2 the character is proved to have been wholly nitrous throughout, and in the other solutions the same was probably the case, at least till near the end of the nitrification. It appears, therefore, that at high temperatures, or, in the case of strong solutions, at low temperatures, the character of the nitrification is at first solely nitrous, while in the case of weak normal solutions at low temperatures nitric acid only is produced. Is this difference to be attributed to the more rapid consumption of oxygen at high temperatures and in strong solutions, coupled with the smaller solubility of oxygen in warm liquids, or is the nitrous character of the action mainly due to the bacteria present, whose avidity for oxygen, and power of reducing nitrates to nitrites have been already studied? That the production of nitrous acid is due to some limitation in the quantity of available oxygen hardly seems a perfectly satisfactory explanation; at least the amount of oxygen consumed seems to have been at times far less than that which the amount of action at other times proved to be available. Thus the oxygen consumed by the warm strong solutions was clearly equally available for the cold strong solutions, yet the latter daily consumed less than half this quantity, though still producing only nitrous acid. The production of nitrous or nitric acid seems to depend in part upon the condition of the ferment. Of this we have had an illustration in the case of bottle C, and further evidence will be forthcoming.

In the solutions nitrified at moderately high temperatures we have fresh illustrations of the different manner in which nitrification may conclude. It would seem that when the ammonia disappears before the nitrous acid is converted into nitric, the nitrites left in the solution are very slow in undergoing change. When, however, the oxidation of the nitrites sets in before the ammonia has been all consumed, the conversion into nitrates is accomplished with surprising rapidity. This view has not yet however received an experimental proof.

The rate of oxidation in these solutions is seen to be from two and a-half to five times greater than in the case of those nitrified at a lower temperature. The rates marked with an asterisk are calculated from the ammonia disappeared, the remainder from the nitrogen found to be oxidised. The former method will give results a little higher than the latter. Solutions of different strengths, but of similar constitution, appear to nitrify at 30° at almost the same rate, the daily oxidation being apparently a little greater in the stronger solutions. The variation in the rate of oxidation as the action advances is best seen in the case of E2 and E4. It must be recollected, however,

that the figures in these cases simply represent oxidation to nitrous acid. If we assume that the hydrogen of the ammonia is oxidised at the same time as the nitrogen, then 1 mol. of nitrogen will require 3 mols. of oxygen to produce nitrous acid, and 4 mols. to produce nitric acid.

We have, lastly, to consider the evidence afforded as to the relation which the nitric acid produced bears to the ammonia originally present. The results obtained in earlier series will be here included.

The determinations of the quantity of nitric acid formed were made by means of indigo, the absence of nitrous acid being previously ascertained by testing with iodide of potassium and starch. A number of determinations were also made by the Crum-Frankland method. These, as already described (p. 376 of this volume), gave at first results far below the truth, but when the use of sulphate of silver was abandoned the results agreed fairly with those obtained by indigo. The following are the comparative determinations made after silver was omitted:—

Nitrogen as Nitric Acid per Million of Solution.

Bottle.	By indigo.	As nitric oxide.	Bottle.	By indigo.	As nitric oxide.
C2	18·7	18·8	E2	182·5	185·5
D2	20·0	19·6	E3	170·7	171·5
D3	143·7	140·1	E4	169·5	170·0
E	20·2	18·5	—	—	—

In some cases the quantity of nitric acid found per million exceeded the ammonia originally present. This was due to the concentration of the solutions by evaporation, and was most perceptible where the nitrification had been long continued, and at a high temperature. To obtain a correction for this error determinations of chlorine were made in the nitrified solutions, from which the amount of concentration which had taken place since the commencement could easily be calculated.

In the following table the proportion of nitrogen originally present as ammonia has been corrected for the error due to concentration in all cases marked with an asterisk. The nitric acid determinations given are, for uniformity, those obtained with indigo, except in the case of D4, which was analysed solely by the Crum-Frankland method:—

Bottle.	Nitrogen per million		Nitrogen obtained as nitric acid for 100 as ammonia.
	Originally present as ammonia.	Obtained as nitric acid.	
BD2	20·5	18·7	91·2
BD4	20·5	19·1	93·2
C	20·5	19·1	93·2
C2	20·5	18·7	91·2
D2	20·9	20·0	95·7
D3	169·7*	143·7	84·7
D4	170·5*	158·0	92·7
E	20·9	20·2	96·7
E2	191·9*	182·5	95·1
E3	179·8*	170·7	94·9
E4	182·5*	169·5	92·9
Mean of 10, excluding D3			93·7

In no case do we obtain the whole of the ammonia in the form of nitric acid. A part of the nitrogen has doubtless become a constituent of the living organisms—the nitrifying ferment and bacteria—present; whether the whole loss is thus to be accounted for, it is impossible to say. In the case of E2, E3, and E4, where increasing proportions of tartrates and of bacteria were present, the product of nitric acid is greatest where the organic matter is least, and least where the tartrates and bacteria were most abundant.

In BD2 and BD4, a small growth of mould in the earlier stages may account for some loss of nitrogen. In C and C2 the indigo determinations may be somewhat below the truth owing to the presence of sugar. I am at a loss to account for the serious deficiency observed in D3, which is not shared by the duplicate experiment D4.

Fifth Series. Bottles H.

This short series of experiments related solely to the influence of light. It had been found that a temperature of 40° was inimical to nitrification, it appeared therefore possible that the effect of sunshine might be due in part to the high temperature which it produced. This idea received strength on finding that a pint bottle of water, placed behind a south window, and exposed to four hours of bright sunshine in July, rose in temperature 17°, and stood at the end of the four hours at 40°·2.

Experiments were then made with a screen of alum-water, and with one filled with a strong solution of sulphate of aluminium. The screen consisted of a glass photographic bath, a foot square, with a space 1 inch in width for fluid; this was filled with the heat-absorbing solution, and placed against the window. The bottles placed behind

the screen were protected from any side radiation by screens of white paper. It was found that after full exposure to bright sunshine, a bottle behind a screen of sulphate of aluminium was 5°·4 lower in temperature than one unprotected. Another bottle behind the screen, but protected entirely from light, stood, however, 6° lower than that receiving filtered light; the screen was thus only partially effective.

On July 13, 1878, three pint bottles of pale-green glass were two-thirds filled with a weak solution of normal composition; the solution had been prepared on March 1, and formed part of the preceding series; it had not yet received carbonate of calcium, or seed. Nitrification had already commenced in this solution (compare duplicate bottles F2′ and E3′, last series), though this fact was not at first known. The three bottles now received carbonate of calcium, and each was seeded with 5 c.c. from bottle G. They remained five days in a dark cupboard, and on July 18 bottle HD was placed behind the screen, protected from all light by a double covering of paper; bottle HL was also behind the screen, but fully exposed to the light passing through it; bottle HLL stood in the same window, but exposed to full sunshine. The subsequent history of these solutions will be gathered from the following table:—

Date.	Interval.	Bottle HD.		Bottle HL.		Bottle HLL.	
		Ammonia.	Nitrogen as nitrous acid per million.	Ammonia.	Nitrogen as nitrous acid per million.	Ammonia.	Nitrogen as nitrous acid per million.
1878.							
July 13	—	—	—	—	—	—	—
„ 18	5 days	—	7·9	—	2·8	—	9·6
„ 29	11 „	considerable	5·2	—	6·9	—	11·4
Aug. 5	7 „	none	none	trace	8·8	considerable	14·0
Sept. 4	30 „	—	—	—	6·9	trace	20·1
„ 19	15 „	—	—	—	6·9	—	19·2
Oct. 5	16 „	—	—	—	6·9	—	19·2
1879.							
April 17	163 „	—	—	—	2·6	—	12·2

All these solutions were fully half nitrified when placed in the window; more nitric and less nitrous acid had been produced in HL than in the others. Nitrification was soon completed in all the solutions: that in the dark nitrified first; that behind the screen of sulphate of aluminium very soon after; that exposed to unfiltered light decidedly later. The chief point of interest is the exclusively nitrous character of the action in both bottles exposed to light, and the extraordinary permanence of the nitrites formed. A green growth was

observed in HL on September 4, and in HLL on April 17. The total nitric acid produced in HD was equal to 22·4 parts of nitrogen per million.

These experiments again leave the effect of light very uncertain.

Sixth Series. Bottles J—K.

This series was also mainly devoted to studying the influence of light; some experiments on the possibility of nitrification without seeding being included.

Five bottles, J, J2, JD, JL, and JLL were partly filled with a normal solution, the constituents of which were in similar proportion to that used for E3 in the fourth series of experiments, but of one-fourth the strength. Three other bottles, KD, KL, and KLL were partly filled with a perfectly similar solution, in which acid tartrate of potassium was used in place of Rochelle salt, and sulphate of calcium in place of sulphate of magnesium. Carbonate of calcium was added to every bottle.

For the first time in these experiments the bottles with their solutions were all maintained for one hour at the temperature of boiling water to destroy any germs that might be present. On the next morning, August 11, 1878, the stoppers were removed, 2 c.c. from bottle AL added as seed to all the bottles save J and J2, and the mouths of the bottles plugged with baked cotton wool. Bottles J, J2, JD, and KD were placed in a dark cupboard, and bottles JL, KL, and JLL, KLL, after 24 hours' darkness, were placed in the south window, the two former behind the screen of sulphate of aluminium solution, the two latter not thus protected. The bottles were all of white glass.

The course of nitrification in bottles JD and KD, kept in darkness at the temperature of the air, was as follows :—

Date.	Interval.	Bottle JD.			Bottle KD.		
		Ammonia.	Nitrogen as nitrous acid per million.	Nitrogen daily oxidised per million.	Ammonia.	Nitrogen as nitrous acid per million.	Nitrogen daily oxidised per million.
1878.							
Aug. 11	—	—	—	—	—	—	—
Sept. 5	26 days	abundant.	6·9	—	abundant	6·9	—
„ 19	14 „	„	18·3	0·81	„	17·5	0·75
Oct. 4	15 „	„	24·4	0·41	„	24·4	0·46
„ 21	17 „	distinct	34·1	0·57	distinct	34·9	0·62
Nov. 4	14 „	trace	35·8	0·12	trace	37·6	0·20
Dec. 16	42 „	none	37·6	—	none	38·4	—
1879.							
Mar. 13	87 „	„	37·6	—	„	38·4	—

We have here the remarkable result of a wholly nitrous action, in which the nitrites produced show no disposition whatever to pass into nitrates. The nitrous acid formed was nearly equal to the whole nitrogen originally present as ammonia, namely 41·4 per million.

Bottles JL, JLL, KL, and KLL, exposed to light, failed entirely to nitrify. A minute trace of nitrous acid was early found in JL and KLL, but this never increased. In JL and JLL a green growth developed, the germs being probably introduced when these bottles were opened on September 19. In KL and KLL no growth has appeared beyond a few minute mycelial threads. Bottle KL was placed in a dark bath at 30° on April 16th, nitrification commenced after a time, and was completed by June 16th; if therefore no fresh germs were accidentally introduced, it would appear that the ferment had not been killed by exposure to light. The nitrification was purely nitrous.

Bottle J, which had never been seeded, was allowed to remain untouched till April 29, 1879; the cotton-wool was then removed and the solution examined. No nitrification whatever had taken place. The solution was perfectly clear. More than eight months had thus elapsed without any commencement of nitrification, though all the conditions were favourable, excepting the absence of seed.

Bottle J2 was covered only with muslin; unfiltered air had, therefore, free access. A luxuriant growth of mould soon appeared, but no nitrification took place. The air of the laboratory doubtless contained nitrifying germs, as soil sampling was in progress for many weeks, but mould, as already mentioned, is apparently inimical to nitrification.

Seventh Series. Bottles L.

The behaviour of nitrites in the presence of a nitrifying ferment had appeared in several of the preceding experiments to be subject to great irregularity; in some solutions they had rapidly oxidised into nitrates, while in others they exhibited a remarkable degree of permanence. With the hope of throwing some light on the subject, a few experiments were now made on the nitrification of nitrites.

One gram of commercial potassium nitrite was dissolved in a litre of water, and divided among four bottles. Bottle LD contained this solution without addition. Bottles LD2, LD3, and LL, received in addition the tartrates, phosphates, and carbonate of calcium usually employed in preparing a nitrifiable solution. All the bottles were then heated for one hour to 100°. On the next day, August 11, 1878, LD3 and LL were seeded with 1 c.c. from bottle AL; the bottles LD, LD2, and LD3 were then placed in a dark cupboard, and bottle LL in an east window.

The bottles were examined from time to time up to October 4 (54 days), but no diminution in the quantity of nitrite was in any case apparent; on the contrary, a decided increase was observed in bottle LD2, the nitrate present in the commercial salt being possibly reduced to nitrite. At this date LD3 and LL were freshly seeded with 1 c.c. from bottle D3, in which a rapid conversion of nitrites into nitrates had just been effected. This fresh seeding proved most effectual; the whole of the nitrous acid quickly disappeared from LD3, while the corresponding solution in the light suffered little change. The numerical results were as follows:—

Date.	Interval.	Nitrogen as nitrous acid per million.			
		Bottle LD.	Bottle LD2.	Bottle LD3.	Bottle LL.
1878.					
August 11	—	143·2	143·2	143·2	143·2
September 20..	40 days	143·2	157·2	146·7	141·5
October 4....	14 „	143·2	154·5	143·2	139·7
„ 21....	17 „	141·5	153·7	104·8	136·2
November 11..	21 „	142·3	151·9	47·2	136·2
December 17 ..	36 „	140·6	143·2	none	136·2
1879.					
March 12	85 „	139·9	141·6	„	126·1

Numerous patches of dark-brown mould developed in bottle LD2, and in bottle LL a green growth commenced after the examination on September 20; the slow diminution of nitrite in these two cases is probably due to the production of vegetable matter.

These experiments illustrate the great stability of nitrites in the absence of a nitrifying ferment, and the power of light to prevent the action of a ferment shown by experiment to be perfectly suitable. The great interest of these experiments is perhaps, however, the distinction which they show may exist between two nitrifying ferments. The ferment used as seed on August 11 was quite ineffective for converting nitrites into nitrates; the same ferment was used on the same date for the experiments of the sixth series. Here it proved capable of changing ammonia into nitrous acid, but the nitrites formed remained unconverted into nitrates, thus affording a striking corroboration of the purely nitrous character of this sample of ferment. On the other hand, a ferment taken from a solution rapidly converting nitrites into nitrates was found to exhibit the same nitric character when added to another solution of nitrite.

The account of the experiments made at Rothamsted is now completed. The novelty of the subject can be my only excuse for giving

in detail many experiments, the results of which are rather suggestive than conclusive.

It may be useful to summarise, as briefly as possible, the results arrived at.

1. A solution of ammonium chloride, fully supplied with plant-food, will not nitrify if germs be excluded (J).

2. A solution of ammonium chloride containing phosphate of calcium and sulphate of potassium, but no organic salt or carbonate of calcium, will not nitrify even when seeded (BD).

3. A solution of chloride of ammonium, supplied with phosphates and sulphates, potassium, calcium, and magnesium, with cane-sugar, will not nitrify even when seeded (C).

4. A solution of ammonium chloride, containing tartrate of potassium, in addition to phosphates and sulphates, may nitrify when seeded; but the nitrification takes place very slowly, the salifiable base required being furnished by the gradual decomposition of the tartrate (BD4).

5. Nitrification takes place speedily only when an excess of a salifiable base, as carbonate of calcium, is present. (Compare BD2 with BD4, and C2 with C).

6. Nitrification may occur in solutions in which calcium salts are apparently absent (E3).

7. A proportion of organic carbon (as tartrate) to nitrogen (present as ammonium chloride), equal to 3 : 10 by weight, is sufficient for the purposes of nitrification, and probably a smaller proportion of carbon would suffice (E2, BD3, and BL3).

8. Solutions containing as much as 640 milligrams of chloride of ammonium per litre can be completely nitrified. The limit of concentration, up to which nitrification is possible, is not yet ascertained.

9. Nitrification is not produced by the growth of mould which takes place in a solution containing tartrates (J2 and BD2).

10. Nitrification is not produced by the growth of bacteria; at least bacteria may flourish in solutions of composition suitable for nitrification without nitrification taking place (D3, D4, and G2).

11. Light certainly hinders nitrification; this is shown by every experiment save one (HL). In 12 experiments out of 13, nitrification is prevented, or greatly delayed by exposure to light, or rather to alternate light and darkness. Evidence is, however, at present wanting that the nitrifying ferment is killed by light (DL and KL). In examples of nitrification in light, the nitrites were abundant, even in weak solutions, and very permanent (BL3, HL, and HLL). Further investigation is required.

12. Nitrification will not take place at a temperature of 40°. Prolonged exposure to this degree of heat apparently destroys the ferment (G and G2).

13. The addition of a small quantity of a nitrified solution to an ammoniacal solution of suitable composition is not immediately followed by a perceptible action; a period of rest, often of considerable length, precedes the active work of the ferment. Whether this apparent rest was simply due to the extremely small quantity of ferment added, which till it had greatly multiplied could produce no appreciable effect, or whether the ferment, which was taken in a large majority of cases from an old solution, was really in the passive state, which has been proved to occur in the life history of many low organisms, is at present quite undetermined.

14. An increase in the concentration of the ammoniacal solution is attended by a lengthening of the period of incubation.

15. An increase of temperature, within certain limits, greatly reduces the length of the period of incubation; this period is shorter at 30° than at 20°.

16. The period of actual nitrification, which succeeds the period of incubation, increases in length with the concentration of the ammoniacal solution, and at a fixed temperature the length of this period varies pretty nearly with the degree of concentration, strong solutions taking, however, in proportion to their strength, rather less time than weak solutions; thus, a solution of double strength will require rather less than a double time for its nitrification. Further evidence is necessary to establish this rule.

17. The period of actual nitrification is diminished greatly in length by a rise in temperature. It is not yet proved, however, that this period is shorter at 30° than at 20°.

18. It follows from 16 and 17 that the average rate of oxidation increases up to a certain point with a rise of temperature, and is also somewhat increased with increasing concentration of the solution.

19. The rate of oxidation is not uniform throughout the process of nitrification; it begins slowly, increases in rapidity, and after reaching a maximum again diminishes towards the close. Further evidence is required on this head.

20. The product of nitrification is not uniform; sometimes nitrous, and sometimes nitric acid is produced. A purely nitric fermentation has occurred only in the case of cold dilute solutions nitrified in the dark. In the case of strong solutions, or of nitrification at elevated temperatures, or in the light, the nitrification has been wholly or chiefly nitrous. Cold dilute solutions, in which nitrification has been long checked by the absence of a salifiable base, also assume a nitrous fermentation when a base is introduced (C). Further investigation is needed under this head.

21. It does not appear that the production of nitrous acid is due to a deficiency of available oxygen; at least this is not a sufficient expla-

University of Michigan

nation for all the facts. The production of nitrous or nitric acid seems to depend in part on the condition of the ferment. The subject is as yet very obscure.

22. The nitrites which are produced during nitrification sometimes pass into nitrates with astonishing rapidity during the final stage of the process, and before the ammonia has entirely disappeared. Under other circumstances, they remain unchanged for a long time after all ammonia has been consumed. Light is apparently a condition which prevents nitrites from turning into nitrates (BL3, HL, HLL, and LL). This, like the preceding question, is at present very obscure.

23. The nitrifying ferment in certain conditions seems only capable of producing nitrous acid, and is unable, even in the dark, of converting nitrites into nitrates (JD, KD, and LD3).

24. The whole of the ammonia originally present is not finally obtained as nitric acid; the largest proportion so obtained has been about 96 per cent.; the average of 10 experiments is 93·7 per cent. In one exceptional experiment the product was only 84·7 per cent.

25. A solution of nitrite of potassium will remain, at least for a long time, without change. The addition of tartrates, phosphates, and carbonate of calcium does not produce change. But if to the solution of nitrite, containing the above-named admixtures, a small quantity of a solution be added in which nitrites have lately changed into nitrates, the oxidation of the nitrite is rapidly effected. This conversion of nitrites, by means of an added ferment, takes place apparently only in the dark.

L.—*Examination of Substances by the Time Method.*

Part I. *Hydrates.*

By J. B. Hannay, F.R.S.E., F.C.S.

β-Double Salts.

In a former paper (*Chem. Soc. J.*, 1877, **2**, 381,) an account was given of the method by which the thermal dissociation of a hydrated salt may easily be followed, and it was shown that the isomorphous salts of different metals, although alike in their statical relations, were widely different in their behaviour when undergoing decomposition. As mentioned in that paper, an examination of double salts, the deportment of whose constituents in the free state was known, would be likely to throw some light on the nature of such compounds in showing how

much the combination affected the affinity of the salts for their water of crystallisation. As I have now finished the examination of a sufficient number of double salts to draw some general conclusions, I have the honour of laying the results before the Society.

Since the above paper was published a large number of experiments have been made regarding the effect of variation of the rate of passage of the air over the salt, and also the state of comminution of the salt itself on the rate at which the moisture is evolved, and the following conclusions arrived at. First, when the air is passing in such quantity that it is in sufficient excess to keep the mixture of air and moisture above its dew point at the coolest part of the apparatus, the results are constant, that is to say, any greater flow of air does not increase the amount of moisture carried over, but any considerable decrease in the rate causes a diminution in the quantity of moisture given off. Secondly, as most of the salts examined fuse partially on heating, the effect of pulverisation was nil, and even in those which do not fuse, the difference of rate of evolution of moisture in a coarse powder as compared with a fine one is scarcely discernible. Still all the salts experimented upon were pulverised to apparently the same state of fineness.

The first double salt examined was that of magnesium and zinc, $MgZn(SO_4)_2.14H_2O$, which, owing to the water of crystallisation remaining the same as in the uncombined salts, offers special facilities for examining the effect of combination upon the affinity of the salts for their water. In a double salt, where one salt replaces the water (or a part of it) in the other, the results would have a special and not a general bearing. As an example of how the work was done, I give the original numbers of the determination of this double salt.

Purity of Salt.—Pure sulphates were prepared by two crystallisations, and the double salt then formed by adding saturated cold solutions to each other in the proportions required, and allowing the salt to crystallise over a sulphuric acid desiccator. The crystals obtained were large, and after being dried and crushed, and then air-dried, were analysed by determining their water of crystallisation. 2·4267 grams of salt were heated to about 500° C., and cooled and weighed, when 1·1475 gram was found to be the loss, equal to 47·39 per cent., the theoretical amount being 47·26. This being nearly pure, the drying tube was weighed, some salt placed in it, and the decomposition carried on, with the following results:—

Tube and salt....	26·1375
Tube	21·9540
	4·1835

Time.			H_2O evolved.	Gram per minute.
—	Drying tube A	50·3720	—	—
—	„ B	48·4745	—	—
5′	„ A	50·4845	0·1125	0·0225
15	„ B	48·9505	0·4760	0·0317
20	„ A	51·3775	0·8930	0·0446
15	„ B	49·1115	0·1610	0·0107
15	„ A	51·3915	0·0140	0·0093
45	„ B	49·1180	0·0065	0·0001
1 h. 55 m.			1·6630	

Or in total time and percentage, as stated in my former paper, we have—

Temperature 100°.

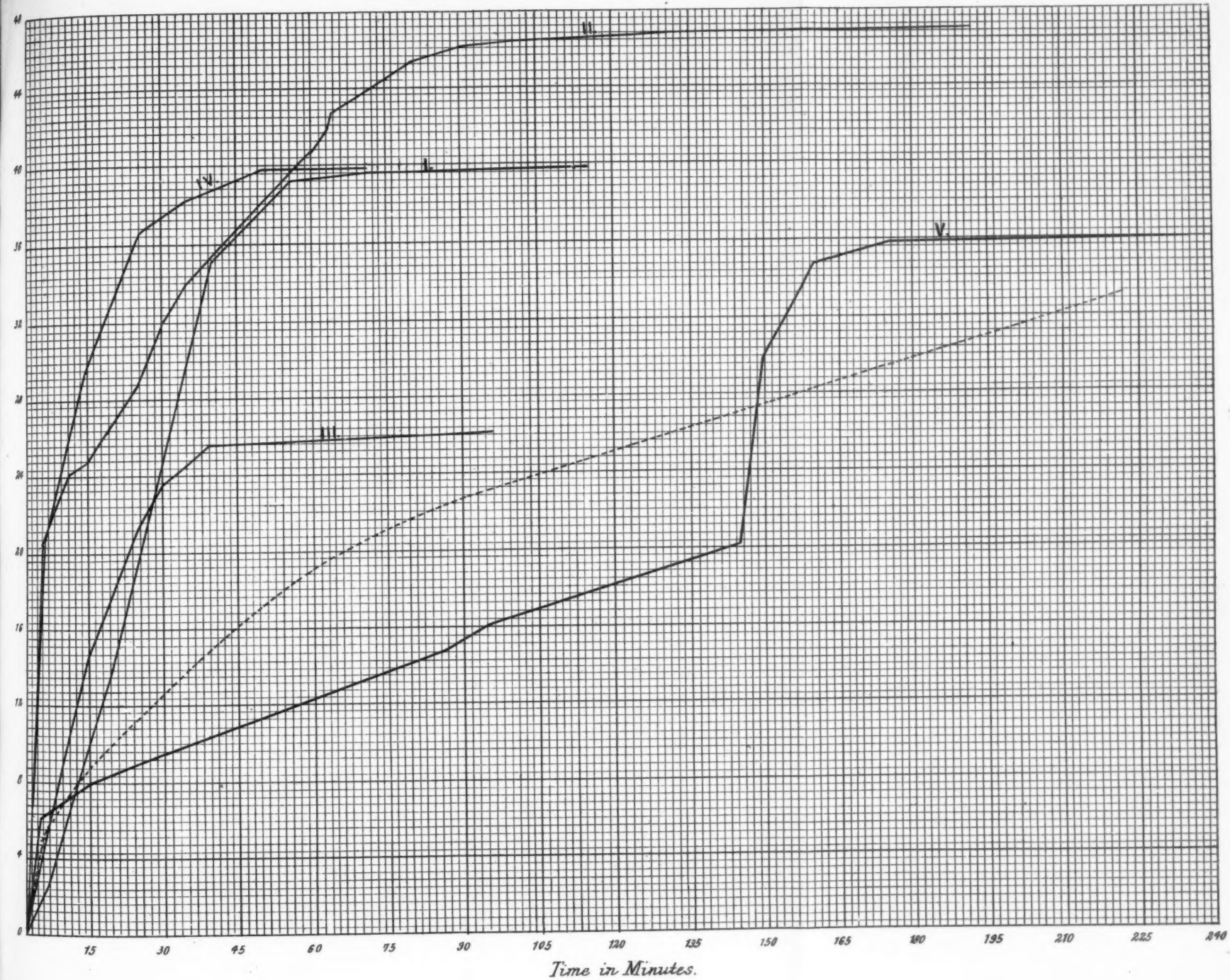
Intervals.	Time.		Loss per cent.	Per cent. per minute.
5′	5′	2·69	2·69	0·54
15	20	11·37	14·06	0·75
20	40	21·35	35·41	1·07
15	55	3·82	39·23	0·25
15	70	0·33	39·56	0·02
45	115	0·15	39·71	0·003

The tube containing the dehydrated salt was found to weigh 24·4715 grams, showing a loss of 1·6660 gram: hence 0·0030 gram had escaped unabsorbed. This being a loss of only 0·16 per cent., was considered correct enough for the object aimed at; in fact the loss was sometimes greater, and yet did not sensibly affect the curve. The course of this decomposition is shown graphically in Curve I. I have also drawn as a dotted line the theoretical course of a mixture of magnesium and zinc sulphates, calculated from the curves given in my former paper. The following table shows the difference between the rate of decomposition of a mixture of the two salts and that of a combination:—

Evolution of H_2O at 100°.

Minutes.	Mixture, $MgSO_4.7H_2O + ZnSO_4.7H_2O$.	Compound, $MgZn(SO_4)_2.14H_2O$.
5′	5·34 per cent.	2·69 per cent.
20	10·51 „	14·06 „
40	14·95 „	35·41 „
55	18·38 „	39·23 „
70	20·68 „	39·56 „
115	24·78 „	39·71, finished.
240	34·65, finished.	

Two conclusions can be arrived at by a glance at these numbers;



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first, that where a *mixture* would leave the compound $MgZn(SO_4)_2.4H_2O$ with evolution of 33·75 per cent. of moisture, the two salts when combined leave a residue $MgZn(SO_4)_2.2H_2O$, with evolution of 40·50 per cent. of moisture, that is, the individuals of the compound hold only one-half of the moisture they can retain when free; and second, that the decomposition is finished in one-half of the time. It thus appears that those two salts in combining have expended one-half of the affinity of the anhydrous salt for its water of crystallisation, and that their combination has been effected in much the same manner as any case of pronounced chemical action. It will be seen from Curve No. I that at first the rate is a little lower than the mixture, but this is due to accidental causes; at 20 minutes the rate is once and a half as quick, while at 40 minutes the rate is more than twice. It is then at one minute reduced to double, and at 115 minutes is less than double. This alteration of the ratio of the rates is caused by the curious property of zinc sulphate in giving off its moisture at an increasing rate, and as the curve occurs in shorter time, the increase takes place at an earlier stage.

The next salt examined was the double sulphate of iron and magnesium, which, as the decomposition curves of the constituents are very similar, seemed likely to offer a good illustration of the effect of combination. The salt was prepared by the same method as the magnesium-zinc salt, and contained 48·25 per cent. of moisture, this being estimated in an atmosphere of hydrogen. The calculated percentage is 48·09. The following table gives the results of its thermal decomposition :—

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5′	5′	20·94	4·19
5	10	23·86	0·58
5	15	24·84	0·19
5	20	26·79	0·39
5	25	29·09	0·46
5	30	31·99	0·58
5	35	34·07	0·41
10	45	36·47	0·24
5	50	37·87	0·28
5	55	39·41	0·30
5	60	40·64	0·24
	Carried on with P_2O_5.		
5	65	42·07	0·28
15	80	45·54	0·23
10	90	46·16	0·06
10	100	46·41	0·02

Carried on with P_2O_5.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
15′	115′	46·60	0·01
15	130	46·78	0·01
30	160	46·89	0·003
30	190	47·01	0·003

As the total water contained in the substance was 48·25, and as the substance on being weighed after decomposition showed a loss of 47·46, we have here the case of a salt giving up all its water at 100°, while its constituents would have retained 3 mols. between them, the magnesium salt two, and the iron one, and we have another confirmation of the law that two salts in combining weaken their affinities for their water of crystallisation, as the water is evolved in one-half of the time. Curve No. II graphically depicts the decomposition.

An interesting case for examination is afforded by the double salts formed by copper sulphate, which, although in the free state a pentahydrate, takes up 2 mols. of water in combining with heptahydrates, forming double salts of the formula $M''M''(SO_4)_2.14H_2O$. As copper sulphate had not yet been examined, its decomposition was done with the following results :—

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
15′	15′	14·45	0·96
5	20	17·29	0·57
5	25	21·16	0·77
5	30	23·48	0·46
10	40	25·54	0·11
10	50	25·60	0·01
10	60	25·70	0·01
15	75	25·95	0·01
10	85	26·14	0·02
10	95	26·20	0·006

The decomposition of this salt was carried no further, the rate decreasing so much that it showed the well known fact of the retention of 1 mol. of water at 100°.

The curve No. III shows that when 2 mols. (14·33 per cent.) of water have been driven off, the rate decreases till 3 mols. have been given off, when the rate shows a quick and continuous decrease till the fourth mol. has been evolved. The curve points to the existence of the two hydrates, $CuSO_4.3H_2O$ and $CuSO_4.2H_2O$ before the greenish-white monohydrate is reached.

To show the agreement between experiments made at different times with the same salt by this apparently rough method of investi-

gation, I give two other determinations of copper sulphate taken at random from several I have done.

I.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
10′	10′	10·95	1·095
10	20	17·17	0·622
10	30	23·52	0·635
10	40	25·62	0·210
10	50	25·72	0·010
10	60	25·81	0·009
25	85	26·18	0·010
10	95	26·22	0·004

II.

15	15	14·04	0·936
10	25	21·08	0·704
25	50	25·54	0·179
20	70	25·82	0·014
25	95	25·99	0·007
10	105	26·01	0·000
5	110	26·07	0·000

This will suffice to show to what extent the process may be relied upon, and on plotting these two tables as curves they will be found to be coincident with the curve given for the former table.

The first double salt of copper sulphate examined was the compound with magnesium sulphate, $CuMg(SO_4)_2.14H_2O$, with the following results. See also Curve IV.

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5′	5′	20·38	4·07
10	15	29·45	0·91
10	25	36·50	0·70
10	35	38·22	0·17
15	50	39·72	0·10
20	70	39·94	0·01

Here we see that the 2 mols. of water which the copper sulphate took up in addition to its real water came off together with 2 mols. from each of the salts in the first five minutes. Here again we see a confirmation of the fact that half the affinity of the salt for its water is lost in the combination, because each salt gives up 2 mols. instead of one in the first five minutes, besides the extra water of the copper sulphate, a loss of 6 mols. requiring 20·32 per cent. The water is also evolved in half the time or at double the rate, and the residue contains only 2 mols. of water.

The next salt examined was the compound of copper sulphate with zinc sulphate, $Cu3Zn(SO_4)_4 28H_2O$, in which as the zinc predominates we ought to find a curve approximating much more closely to the zinc curve than to the copper. This salt was chosen for the reason that it would show whether the force holding the zinc salt to its water was diminished by one-half or only by one-fourth, as the first would mean that the compound was a combination of 1 zinc mol. with the copper, and the two other zincs with each other, while the second would indicate that the three zincs were equally united with the copper. The following are the results. Curve V.

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5′	5′	6·18	1·23
5	10	7·10	0·17
5	15	7·94	0·17
10	25	8·92	0·098
30	55	11·84	0·097
30	85	14·80	0·098
10	95	16·01	0·121
20	115	17·72	0·085
30	145	20·14	0·081
5	150	29·64	1·90
10	160	34·79	0·515
15	175	35·78	0·066
30	205	35·92	0·005
30	235	35·95	0·000

By a comparison of these numbers with the curves of copper and zinc, we see that as in the magnesium-copper salt the first few molecules are given off very easily, doubtless owing to the evolution of the two molecules in excess in the copper sulphate, and that the residue contains fully five molecules of water, seeming to approximate to the body $CuZn(SO_4)_2 2H_2O + 2ZnSO_4.2H_2O$, that is, the state of the salt when decomposing seems to be a simple double sulphate of copper and zinc associated with two molecules of zinc sulphate. The two zinc sulphate molecules seem to have been little affected by the combination, as they return nearly the same amount of moisture which they do in the free state. As was to be expected, the weak affinity with which the water of the double salts is held, the curves show few sudden changes to mark out various hydrates, but curve No. V shows the individuality of the zinc salt showing plainly in spite of its combination with copper.

It may be objected that it is not known that a mixture of two salts on being heated would give off the moisture at a rate which

is the mean of the two, and in most cases this cannot be proved, as the salts fuse on being heated, and will thus form a combination. However, neither the copper nor the magnesium salt fuses on being heated, so a mixture of these two sulphates was treated as the double salt had been, with the following result :—

Temperature 100°.

Intervals.	Total time.	Loss per cent.	Per cent. per minute.
5″	5′	6·04	1·21
20	25	14·15	0·405
10	35	17·07	0·584
30	65	25·92	0·295
30	95	28·74	0·094
30	125	29·82	0·036
30	155	30·00	0·006
30	185	30·09	0·003

Comparing this with the table on page 461, we see that the moisture in the true double salt is given off at a rate fully twice as fast as that from the mixture, showing that by combination the affinity of the anhydrous salt for its water of crystallisation has been weakened.

Conclusion.—Two hydrated salts in forming a double salt containing the normal amount of water, expend one half of the affinity of the anhydrous salt for its water of crystallisation in combining with each other, showing that the formation of double salts is comparable with other forms of chemical action.

My thanks are due to Mr. David Stewart for his kind aid in assisting me in these experiments.

LI.—*On the Volumes of Liquids at their Boiling Points, obtainable from Unit-Volumes of their Gases.*

By William Ramsay, Ph.D., Tutorial Assistant of Chemistry in the University of Glasgow.

As long ago as 1855, Kopp pointed out that the specific gravities of organic compounds show a certain regularity with regard to each other. By dividing the molecular weights of compounds by their specific gravities at their boiling points, he obtained a series of numbers, which he termed at first atomic, or molecular volumes, and subsequently specific volumes; these numbers bear a certain relation to one another, and for homologous series of carbon compounds show a regular increase.

Kopp's method of determining the volume of a liquid at its boiling point (one of the points at which volumes are comparable, for at that

point the vapour-tensions of all liquids are equal) was to ascertain that point accurately, to determine the specific gravity of the liquid at some known temperature, and having experimentally discovered the coefficient of expansion of the liquid, to calculate its volume from these data. Up to the present time, this process has remained the only one, and although probably capable of yielding the best results, it involves the use of complicated and expensive apparatus, and necessitates laborious calculation.

An easy method of determining the specific gravities of liquids at their boiling points is much to be desired, for much light is thereby thrown on the constitution of the compound.

Before describing an apparatus which has been found very suitable for this purpose, it may perhaps not be out of place to inquire: what are the precise conceptions involved in the expressions, *atomic volume*, *molecular volume*, and *specific volume*, as used by Kopp and numerous other writers?

It is evident that,

$$\frac{\text{Weight}}{\text{Specific gravity}} = \text{volume},$$

consequently,

$$\frac{\text{Molecular weight}}{\text{Specific gravity of molecule}} = \text{molecular volume}.$$

But the specific gravity of a molecule of a liquid cannot be determined, for equal volumes of different liquids do not contain equal numbers of molecules. The same remark applies to the expression *atomic volume*.

The term *specific volume* appears to me to be a misleading one when used in the sense given it by Kopp. When we speak of specific gravity, we mean the weight of a bulk of some specified substance compared with the weight of the same bulk of water, or some other standard. By specific rotatory power, is implied the power of a known thickness of some specified substance to impart a specified rotation to polarised light, and so with other examples. From analogy, specific volume should be the reciprocal of specific gravity, for volume varies inversely as density. This use of the phrase does not correspond to the sense in which it is understood by Kopp. In his nomenclature, specific volume represents the product of real specific volume (reciprocal specific gravity) into molecular weight, thus:—

$$\text{Specific volume (Kopp)} = \frac{\text{Molecular weight}}{\text{Specific gravity}}.$$

Now what is implied here by molecular weight? Evidently the specific gravity of the gas, the standard being hydrogen at 0°, for the weights of the molecules of two gases are supposed to be proportional

to the weights of equal volume of these gases, from Avogadro's hypothesis. The specific gravity of the *liquid*, however, is referred to water at 0°. Here two scales are employed, viz., that based on twice the weight of hydogen as unity, and that in which the weights of the substances are compared with water at 0°.

The number obtained from the above equation may and does show relations between different substances, but represents no relation between the volumes or weights of liquids at their boiling points and that of the gases obtainable from those liquids. This has been alluded to by Groshaus (*Ann. Chem. Pharm.*, **116**, 221). But if the number representing the specific gravity of the liquid at its boiling point be multiplied by the specific gravity of water at 0° referred to half the weight of hydrogen gas at 0°, then the specific gravities of both liquid and gas are commensurable, for they are on the same scale. That number is 22,326. By dividing the specific gravity of the gas by that of the liquid, we obtain the ratio of the specific gravity of the liquid to that of the gas; or, conversely, the ratio of the specific volume of the gas to that of the liquid, both referred to the volume of gaseous hydrogen at 0° as unity.

Now, in the case of the carbon compounds, as the molecular weight increases, the specific gravity of the gas increases, and the specific volume of the gas decreases; and with increase of molecular weight, the specific gravity of the boiling liquid decreases (as a general rule) and its specific volume increases; increase of molecular weight therefore increases the number representing the ratio between the specific volume of the gas and that of the liquid. *That ratio when both hydrogen and water standards are employed, is what Kopp terms specific volume.* It is not the case, that by increase of molecular weight, the real specific volume, that is, the real volume of unit-weight of the boiling liquid, is necessarily increased; for instance in the homologous series of the C_nH_{2n} group, the true specific volume is the same for all the members. But the ratio between the true specific volume of the gas and that of the liquid is increased, and regularly corresponding to regular increase of molecular weight.

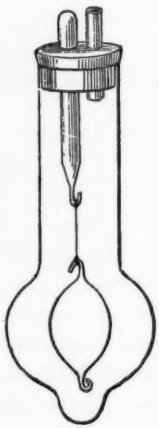
From what has been said, it is evident that by reversing Kopp's process, by dividing the specific gravity of the boiling liquid by that of the gas, the ratio of volume of liquid to that of gas is obtained; or in other words, the amount of gas obtainable from unit-volume of liquid. Kopp's numbers, therefore, if translated into the gaseous hydrogen standard, represent the volume of liquid at its boiling point, obtainable from unit-volume of gas. As hydrogen is accepted as the unit of gaseous density, it must necessarily be adopted as unit in specific volume, using the term in Kopp's signification. Now, the specific volume of liquid hydrogen is 5·5, according to Kopp; and the

specific gravity of liquid hydrogen is $\frac{1}{5{\cdot}5} = 0{\cdot}1818$. Now $0{\cdot}1818 \times 22{,}326 = 4{,}059{\cdot}2$. That number is the specific gravity of liquid hydrogen referred to gaseous hydrogen as unity. Dividing therefore the specific gravity of gaseous hydrogen, 1, by 4,059·2 (specific gravity of liquid hydrogen) we obtain the number 0·00024635. To avoid the decimal figure, it is convenient to represent the volume of liquid obtainable from 10,000 volumes of gas. That number is sufficiently accurately assumed to be 2·46. The corresponding numbers for some other elements are:—

Carbon	4·92	Chlorine.....	10·20
Oxygen	3·49 or 5·45	Bromine.....	12·44
Sulphur.....	10·27 or 12·79	Iodine	16·77

It is evident that Kopp's numbers represent the relative amounts of boiling liquid obtainable from 22·326 volumes of gas measured at 0°.

Description of the Apparatus.—The principle of the process to be described is the *direct determination of the weight of a known volume of a liquid at its own boiling point.* The vessel into which the liquid is introduced consists of a thin glass bulb, of which a sketch is given, shaped somewhat like a lemon, capable of holding about 10 c.c. of water. A capillary tube, bent into the form of a hook, terminates the upper portion. The lower part is provided with a similar hook, but solid, and care must be taken in blowing the bulb to make the curve of the glass inside the lower half as even and round as possible. Lead glass is to be preferred, as it gives a bulb with no flaws and air-bells. The capacity of this bulb is accurately determined by filling it with boiled distilled water of known temperature, and weighing it; from the known data of the expansion of water, its volume at 0° is easily calculated. The expansion of the glass is afterwards ascertained by a method which shall be described in its place. The bulb is suspended by means of platinum wires in a species of wide-necked flask of peculiar shape, shown in the annexed drawing, about one third its real size, by means of thin platinum wire, attached to a glass rod, passing through a hole in the cork, which closes the flask. Through another hole in the cork, a glass tube issues, which may be connected with a condenser, if necessary. The flask is clamped at a convenient height above a Bunsen burner, the flame of which must be easily regulated.



The small bulb is filled with the liquid to be examined by gently warming it, and dipping the capillary neck into the liquid. A small amount ascends into the bulb; by boiling the drop of liquid either over a Bunsen flame, or if the liquid is very volatile, by means of hot mercury, and again inserting the open tube into the liquid, the bulb becomes nearly full. It is not necessary to fill it completely; two or three c.c. of the same liquid are then introduced into the flask, and the bulb is suspended in it, as shown in the woodcut. The flask is then heated till the liquid it contains enters into violent ebullition. The volume of the liquid in the bulb is soon seen to increase, and before long drops begin to fall from the capillary neck. The liquid in the flask is kept boiling as long as these drops fall, usually about ten minutes. The heat is then removed, and when the bulb is cold, it is dried and weighed. The weight, minus that of the bulb alone, represents the liquid which filled the bulb at nearly its own boiling point, after correction has been made for the expansion of glass, and the difference between the temperature of the liquid in the bulb and its real boiling point. That correction is represented as a coefficient. It is found by weighing the bulb full of boiled distilled water at a known temperature, and then performing the process just described, water being the liquid. With almost every bulb the coefficient with which to multiply the result found for water so as to make it correspond with the volume found by Regnault or Kopp for water at 100° was 0·00015 for each degree Centigrade. In calculating the specific gravity of a liquid, the following expression was used:—

$$\text{Specific gravity} = \frac{W'}{1 + (0{\cdot}00015 \times TW}.$$

W′ is the weight of the liquid; W, that of the water filling the bulb at 0°; and T, the temperature at which the liquid boils.

There are two cases in which a slight variation of the method of filling the bulb is advisable. If the liquid is decomposed by air or moisture, or if it is very volatile, it is difficult to fill the bulb in the manner described. In such a case, two glass rods are passed through the cork; the platinum wire from one is attached to the capillary neck, and the wire from the other is attached to the small ring of glass at the other side of the bulb. The bulb is heated to the boiling point of the liquid, and when a sufficient amount of air has been expelled, its neck is lowered below the level of the liquid in the flask; as it cools, some liquid enters. The neck is then raised, and the liquid in the flask is again boiled. Its vapour raises the temperature of the liquid in the bulb, which emits vapour, while air is expelled. The neck is again dipped into the liquid, and as soon as the whole apparatus has cooled, the bulb is full. The rest of the operation does not differ from what has already been described.

The bulb may be easily emptied by suspending it in the flask with the capillary neck downwards, and boiling the contents of the flask.

The time usually required for one determination is half-an-hour. The bulb is cleaned by washing it with a few drops of alcohol, and driving out the vapour by heat. It is then washed with the substance under examination three or four times, and after the liquid has been converted into vapour in the same manner, the bulb may be considered clean. A small ring of copper wire was found of service for holding the bulb while filling it.

In giving the following results of determinations of specific volumes of liquids at their boiling points, preferably called "ebullition-volumes," it is of advantage to state the number of determinations made with one liquid. As an example of the concordance between several determinations of the specific gravity of one substance, I may choose the following at random:—

Phenol:—Weighings.....	I.	6·598	grams.
	II.	6·591	,,
	III.	6·595	,,
Ethyl alcohol:—Weighings.....	I.	5·198	,,
	II.	5·205	,,
	III.	5·200	,,
Amylene:—Weighings.....	I.	4·451	,,
	II.	4·448	,,
	III.	4·457	,,
	IV.	4·453	,,

The mean of these numbers has always been taken, unless a manifestly incorrect result has been obtained; this happened occasionally with some liquids, especially nitro-compounds and nitrates, which decompose at temperatures a little above their boiling points; they are apt to evolve gas before they boil, and some liquids are liable to spurt out of the small neck of the bulb, owing to capillarity during cooling. In such cases, the best determinations are given:—

In the following tables of ebullition-volumes determined by means of the apparatus described, Kopp's method of expression shall be given for convenience of reference. The calculated numbers are taken from his determinations, and are:—

Hydrogen.....	5·5	Sulphur	28·6
Carbon	11·0	Chlorine	22·8
Oxygen.....	7·8	Bromine	27·8
,, ...	12·2	Iodine	37·5
Sulphur	23·0		

TABLE I.—*Hydrocarbons.*

	Boiling point.	No. of experiments.	Sp. gr. at b. p.	Vols. of liquid from 10,000 vols. of gas at 0°.	Sp. v. (Kopp) found.	Sp. v. calculated.
Amylene, C_5H_{10} ..	35°	4	0·6319	49·62	110·8	110
Hexane, C_6H_{14} ...	60·8	1	0·6199	62·13	138·7	143
Heptane, C_7H_{16} ..	91	1	0·6060	73·90	165·0	165
Benzene, C_6H_6 ...	80	4	0·8142	42·91	95·8	99
Toluene, C_7H_8 ...	111	2	0·7650	53·87	120·5	121
Xylene, C_8H_{10} ...	132—134°	2	0·7335	64·72	144·5	143

Of the numbers in this table, two, those of hexane and benzene, alone differ much from the calculated numbers. I have to express my indebtedness to Professor Schorlemmer for the loan of the samples of hexane and heptane. The amylene, benzene, and toluene were obtained from Herr Kahlbaum; they boiled with absolute constancy at the temperatures given in the table, and their refractive indices for the D line were found to coincide exactly with determinations by Dr. Gladstone. The xylene is a mixture of two isomerides, fractionated from coal-tar, and is not absolutely pure.

On finding benzene to give a result differing so materially from the calculated one, I exposed it to cold so as to freeze it, and the crystals were collected, melted, and redistilled. There was no difference in the boiling point nor in the specific gravity at that point. The four weighings are (1) 5·713; (2) 5·713; (3) 5·714; and (4) after freezing, 5·716 grains. Kopp gives his determination of the specific volume of benzene as 96·0. These irregularities open up a question which has been referred to by Tschermak, and shall be discussed further on.

TABLE II.—*Compounds containing Carbon, Hydrogen, and Oxygen.*

	Boiling point.	No. of experiments.	Sp. gr. at b. p.	Vol. of liquid from 10,000 vols. of gas at 0°.	Sp. v. (Kopp) found.	Sp. v. calculated.
Ethyl alcohol, C_2H_6O ..	78°	3	0·7339	28·07	62·7	62·8
Octyl alcohol, $C_8H_{18}O$ ..	181	2	0·6589	88·38	197·3	194·3
Ethene glycol, $C_2H_6O_2$ ..	195	3	0·9444	29·40	65·6	70·6
Acetic aldehyde, C_2H_4O .	21	3	0·7771	25·36	56·6	56·2
Furfurol, $C_5H_4O_2$	162	3	0·9310	46·16	103·0	101·4
Ethyl ether, $C_4H_{10}O$	34·5	2	0·6956	47·65	106·4	106·8
Acetic acid, $C_2H_4O_2$	113	3	0·9325	28·82	64·3	64·0
Valerianic acid, $C_5H_{10}O_2$	195	2	0·7569	60·36	134·7	130·0
Methyl formate, $C_2H_4O_2$	33	3	0·9482	51·53	63·2	64·0
Ethyl formate, $C_3H_6O_2$ ..	55	2	0·8649	69·68	85·6	86·0
Phenol, C_6H_6O	186	3	0·8789	47·90	106·9	106·8

In the above-mentioned compounds it will be seen that oxygen has two values, viz., 3·49 and 5·45 (7·8 and 12·2, Kopp). The hypothesis usually accepted to account for this fact is its different states of combination. Oxygen as it exists in alcohols and ethers, and half the oxygen of the carboxyl group of acids, possesses a different value from oxygen in ketones and aldehydes. It is noticeable that in glycol, $C_2H_6O_2$, both atoms of oxygen, as might have been predicted from its alcoholic character, have the value 3·49. In furfurol, a pyromucic aldehyde, $C_5H_4O_2$, on the other hand, both atoms of oxygen have the value 5·45 (12·2). It was predicable that the oxygen of the aldehyde group should possess this volume, but considerable obscurity still surrounds the manner of combination of the second atom of oxygen. Light is thrown on the subject by its ebullition-volume. In ethers, for example in ethyl ether, $C_2H_5OC_2H_5$, where oxygen is in combination with two separate atoms of carbon, its volume is the same as in alcohol, where it serves to connect carbon with hydrogen; it appears to possess a greater volume only when in combination with one carbon atom. In furfurol both atoms of oxygen have the higher value; it is therefore likely that the atom of oxygen which does not form part of the aldehydic group, —CHO, is combined so as to form a ketonic group, —CO—, or such a group as . It is also noticeable that no difference in volume exists between oxygen in alcohols and phenols, although the two groups differ materially in character.

TABLE III.—*Compounds containing Chlorine, Bromine, and Iodine.*

	No. of experiments.	Sp. gr. at b. p.	Vols. of liquid from 10,000 vols. of gas at 0°.	Sp. v. (Kopp) found.	Sp. v. calculated.
Carbon tetrachloride, CCl_4	2	1·4658	47·06	105·0	102·2
Chloroform, $CHCl_3$	2	1·3954	38·36	85·6	84·9
Ethyl chloride, C_2H_5Cl	1	0·8510	21·42	75·8	72·3
Butyl chloride, C_4H_9Cl	2	0·8094	51·20	114·3	116·3
Amyl chloride, $C_5H_{11}Cl$	2	0·7801	61·14	136·5	138·3
Ethene dichloride, $C_2H_4Cl_2$	2	1·1356	39·04	87·2	89·6
Ethidene dichloride, $C_2H_4Cl_2$	2	1·1070	40·62	89·5	89·6
Benzoyl chloride, C_7H_5OCl	2	0·9857	56·57	126·3	139·5
Amyl bromide, $C_5H_{11}Br$	2	1·0502	64·40	143·8	143·3
Methyl iodide, CH_3I	2	2·1905	29·04	64·8	65·0

For the volumes of chlorine, bromine, and iodine, the numbers 22·8, 27·8, and 37·5 are given by Kopp; on the gaseous hydrogen standard these numbers are 10·2, 12·44, and 16·77. The numbers on the above

table call for no special remark, except that the low result with benzoyl chloride is probably owing to impurities.

Chromium oxychloride, CrO_2Cl_2 may be appropriately introduced here. Only one determination was made.

	Boiling point.	Sp. gr. at b. p.	Vols. of liquid from 10,000 vols. of gas at 0°.	Sp. v. (Kopp).
CrO_2Cl_2	117°	1·7538	39·6	88·4.

The ebullition-volume of chromium in this compound evidently depends on the values assigned to the oxygen with which it is in combination. Now sulphur in carbon disulphide, CS_2, has been shown by Kopp to have two different values; and reasoning from analogy it may be inferred that the two atoms of oxygen in carbon dioxide should have the ebullition-volumes 3·49 and 5·45 respectively. In chromium oxychloride it is nearly certain that oxygen is in direct combination with chromium, for the compound has no resemblance to a hypochlorite. If it be assumed that the two atoms of oxygen have different values—

$$\underset{CrO_2Cl_2.}{39{\cdot}6} - (\underset{O_i.}{3{\cdot}49} + \underset{O_{ii}.}{5{\cdot}45} + \underset{Cl_2.}{20{\cdot}40}) = \underset{Cr.}{10{\cdot}26}$$

$$\{(\text{Kopp})\ 88{\cdot}4 - (7{\cdot}8 + 12{\cdot}2 + 45{\cdot}6) = 22{\cdot}8\}$$

The ebullition-volume of chromium coincides therefore with that of chlorine.

TABLE IV.—*Compounds containing Sulphur.*

	Boiling point.	No. of experiments.	Sp. gr.	Vols. of liquid from 10,000 vols. of gas at 0°.	Sp. v. (Kopp) found.	Sp. v. (Kopp) calculated.
Carbon disulphide, CS_2..	43°	4	1·2176	27·89	62·3	62·6
Sulphur chloride, S_2Cl_2..	138	3	1·4848	40·72	90·9	91·6
Sulphur, S	446	I.	1·4883	19·26	21·5	—
„	—	II.	1·5130	18·99	21·1	—
„	—	III.	1·4592	19·64	21·9	—
„	—	IV.	1·4578	19·66	21·9	—
„	—	V.	1·4787	19·39	21·6	—
Mean	—		1·4799	19·39	21·6	—

The numbers in the third column of figures represent the amount of liquid obtainable from 10,000 volumes of sulphur vapour, measured at 0°. Kopp's "specific volume," given in the fourth column, is the quotient obtained by dividing 32, the atomic weight of sulphur, by its specific gravity. The element sulphur, therefore, in the free state has nearly twice the ebullition-volume that it possesses in combination.

Like oxygen, sulphur has two volumes, supposed to depend on the manner in which it is combined. These are 10·27 and 12·79 (23 and 28·6, Kopp). In carbon disulphide it exists in both states, thus—

C.	+	S.	+	S.	=	CS_2.
4·92		10·27	+	12·79	=	27·98
{(Kopp) 11	+	23	+	28·6	=	62·6}.

In sulphur chloride, on the other hand, it possesses the volume 10·27 (23), for $(10{\cdot}27 \times 2) + (10{\cdot}2 \times 2) = 40{\cdot}94$ $\{(23 \times 2) + (22{\cdot}8 \times 2) = 91{\cdot}6\}$.

When free, sulphur appears to have the ebullition-volume 19·39 (43·2, Kopp). As the apparatus used for determining the specific volume of sulphur differed somewhat from that with which the former determinations were made, a short description may prove of interest.

The bulb was blown of combustion-tubing and had the shape shown in the cut. It was filled with melted sulphur by suction at one of the ends and placed in the wire support in which it rests in the drawing. It was then introduced into a round porous earthenware cell in which some sulphur was melted. An iron lid, with a hole through which the wire passed, closed the top of the cell. A powerful triple Bunsen burner soon caused the sulphur in the cell to boil, and after keeping it in brisk ebullition for about 15 minutes the bulb was lifted out, allowed to cool, and weighed. As the weight of the bulb and its weight with water had already been determined, it was an easy matter to calculate its ebullition-volume.

TABLE V.—*Compounds containing Nitrogen.*

	Boiling point.	No. of experiments.	Sp. gr.	Vol. of liquid from 10,000 vols. of gas at 0°.	Sp. vol. (Kopp) found.	Value of N.	
						H. standard.	(Kopp).
Aniline, C_6H_7N	183°	4	0·8527	48·85	109·1	2·11	4·6
Toluidine, C_7H_9N.....	197	3	0·8302	57·73	128·9	1·15	2·4
Dimethylaniline, $C_8H_{11}N$	190	3	0·7941	68·25	152·4	1·83	3·9
Diphenylamine, $C_{12}H_{11}N$	310	4	0·8293	91·28	203·8	5·18	11·3
Pyridine, C_5H_5N	117	2	0·8617	41·06	91·6	4·16	9·1
Picoline, C_6H_7N.....	134	4	0·8197	50·82	113·4	4·08	8·9
Lutidine, C_7H_9N	154	3	0·7916	60·54	135·1	3·96	8·6
Collidine, $C_8H_{11}N$	173	2	0·7839	70·74	157·9	4·32	9·4
Pyrrol, C_4H_5N	133	3	0·7276	41·10	92·1	9·12	20·6
Azobenzene, $C_{12}H_{10}N_2$ ..	293	3	0·8256	98·72	220·4	7·54	16·7
Propionitrile, C_3H_5N....	97	3	0·7017	35·11	78·4	8·05	17·9
Benzonitrile, C_7H_5N....	192	4	0·8330	55·39	123·7	8·65	19·2
Ethyl nitrate, $C_2H_5NO_3$.	87	2	0·9991	40·80	91·1	8·19	18·2
Nitrobenzene, $C_6H_5NO_2$.	220	1	1·0210	54·44	121·5	5·64	12·4

As has been shown by Kopp and others, the value of nitrogen varies in different compounds. Kopp's values, expressed in his own standards, are 2·3 for nitrogen in amines, 17 in cyanogen compounds, and 17·4 in NO_2. It will be seen, on referring to the table, that a higher value than 2·3 was found for nitrogen in amines; omitting diphenylamine, which, from its very high boiling point, is difficult of determination, the mean value from aniline, toluidine, and dimethylaniline is 3·6. The aniline employed was carefully distilled and boiled with absolute constancy at 183°. The four determinations were remarkably concordant. It must, however, be acknowledged that the difference between Kopp's number and that found by me lies within experimental error.

The ebullition-volume of the pyridine series of bases is now, so far as I am aware, published for the first time. The results from the four bases, pyridine, picoline, lutidine, and collidine, agree closely with one another. The mean value of nitrogen in the hydrogen standard is 4·13, and on Kopp's standard 9·0. The difference between the ebullition-volume of these bases and their isomerides of the aniline series is very striking.

Pyrrol is also now given for the first time. From its volume it appears to belong to the cyanogen group, or at least to approach nitriles in constitution.

Azobenzene also appears to resemble cyanides and nitrils. From its high boiling point it is not impossible that the number representing the value of nitrogen should really be 17. In the case of pyrrol, however, a perfectly pure sample was used, and I am inclined to think that in it nitrogen possesses a value distinct from those of its other compounds. Pyrrol is at least proved to have little analogy in constitution to the pyridine group.

In calculating the value of nitrogen in ethyl nitrate, Kopp has been followed as regards the value assigned to oxygen. The lower value, 7·8, has been chosen. There is no reason for supposing that oxygen has that value; by substituting other values, nitrogen becomes 9·4, 5·0, or 13·8, in Kopp's numbers.

The specific gravity of nitrobenzene at its boiling point was very difficult to determine and is probably incorrect, for that body decomposes at a temperature very little above its boiling point.

Such are the results of the determinations of ebullition-volumes by means of the apparatus described. On the whole, they give results remarkably in concordance with those obtained by Kopp. In comparing different bodies with one another, however, differences are observed much greater than those of separate determinations with the same body. There are two possible causes for this anomaly.

First. The substances examined may not have been quite pure.

Second. The boiling point may not be a fit point of comparison. Tschermak (*Ann. Chem. Pharm.*, **114**, 31) states that several substances, alcohol, water, and carbon disulphide among others, do not exhibit the same regularity at lower vapour-tensions than that necessary to overcome atmospheric pressure—that at the boiling point. May it not be the case that ebullition-volumes are more in accordance with a general law at high than at low vapour-tensions? A somewhat similar instance is to be found in the case of the specific heats of silicon and carbon, which become comparable with those of the other elements only at a high temperature.

Third. The elements may not possess the same value in different compounds. When it is stated that carbon has the ebullition-volume 4·92, or, as Kopp expresses it, the specific volume 11, all that is affirmed is that one substance, A, containing an atom of carbon more than another substance, B, and consequently possessing a molecular weight greater than that of B by 12, or a vapour-density greater than that of B by 6, condenses to form a liquid greater than that obtained from 10,000 volumes of B in the state of gas by 4·92 liquid-volumes. It is of course impossible to infer that 10,000 volumes of gaseous carbon condense to form 4·92 volumes of boiling liquid carbon. Buff (*Ann. Chem. Pharm.*, Suppl. 4, 129) has made experiments on unsaturated hydrocarbons with the view of ascertaining whether they agree with saturated hydrocarbons in specific volume. His results are not conclusive, for the difference is within the amount of variation from experimental error, but appears to show that the value of carbon is not absolutely constant. It may be the case that the value of carbon depends on its mode of combination, as appears to hold with oxygen, sulphur, and nitrogen, but that its variation is slight in comparison with the latter elements. And when we regard the enormously different values assigned to nitrogen in compounds possessing the most varied properties, it is impossible to avoid the supposition that the value of nitrogen itself cannot undergo such enormous modification, but that the part which it plays is to influence the value of all the elements with which it is in combination. It is clear that in the process of formation of two such bodies as aniline and picoline very different amounts of heat must be evolved; it is therefore to be expected that the condensation should differ in the two instances, and that the ebullition-volumes of these two bodies should also differ from one another.

LII.—*Third Report to the Chemical Society on "Researches on some Points in Chemical Dynamics."*

Section I. By C. R. Alder Wright, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School, and A. P. Luff.

Sections II, III, and IV. By C. R. Alder Wright and E. H. Rennie, M.A. (Sydney), Demonstrator of Chemistry in St. Mary's Hospital Medical School.

§ 1. *Determination of Relations existing between Rate of Reduction of Copper Oxide by Hydrogen, Time, and Temperature.*

It was incidentally shown in Reports I and II that when determinations are made of the amounts of oxygen removed from various metallic oxides at temperatures somewhat above the "points of initial action" (as found by periods of exposure to the action of reducing agents of some minutes only) numbers are obtained constituting the data for the construction of curves giving by inspection the ratios between the deoxidation taking place at varying temperatures in a given time (15 minutes say) and the temperatures themselves. Evidently by carrying out analogous experiments at constant temperatures for varying times, the other conditions of the experiments being as nearly as possible identical, other curves would be obtained giving the ratios between the amounts of deoxidation at given temperatures and the times requisite to produce these amounts of deoxidation. These two sets of curves can obviously be combined so as to form a curved surface related to three planes mutually at right angles, so that the lengths of the perpendiculars let fall upon these three planes from any given point on the surface shall represent respectively a given amount of deoxidation and the time and temperature requisite to produce that deoxidation under otherwise constant conditions.

Planes cutting this surface and parallel to one of the three given primary planes will then give intersections representing the curves for deoxidation and temperature, time being constant; other planes parallel to a second of the three primary planes will similarly give intersections representing the second set of curves for deoxidation and time, temperature being constant; whilst planes parallel to the third of the three primary planes will give intersections representing curves indicating the relative times and temperatures requisite to produce given constant amounts of deoxidation.

Given a series of curves indicating for various times T_1, T_2, T_3 . . . .

(constant for each curve) the relation between deoxidation and temperature, the curved surface can be drawn and the second and third sets of curves deduced therefrom. Or, given a series of curves indicating for various temperatures t_1, t_2, t_3 .... (constant for each curve) the relations between deoxidation and time, the curved surface can similarly be drawn and the first and third sets of curves thence deduced. As at first sight it appeared to be, for various reasons, more convenient to observe the curves of the second kind than those of the first, this mode of arriving at the curve-surface was adopted.

The use of paraffin, air, or other analogous baths, even when fitted with Page's mercurial regulator* (which we found to work far better than any other kind tried), was found to be far less convenient for obtaining sensibly constant temperatures for considerable periods of time than the employment of vapour-baths obtained by heating uniform substances in cohobating arrangements; such substances as glacial acetic acid, turpentine hydrocarbon, aniline, naphthalene, mercury, &c. (purified when requisite by previous fractional distillation), were therefore employed in nearly every one of the observations made. For temperatures above 100° Page's regulator was found to have the disadvantage that, after some hours or days' use, the mercury volatilised in sensible quantity, thus lowering its level and allowing more gas to pass, and consequently raising the temperature of the bath in which it was immersed: even at 85° this action was noticeable after a week or two. The exact temperature of the vapour-bath used was taken by means of thermometers carefully compared with a Kew-standardised thermometer, the upper part of the stem of which was carefully calibrated so as to give a table of readings based on the Kew-standardisation up to 100° C. In some cases the temperature rose slightly through oxidation (as with aniline) or volatilisation of more volatile portions; but the errors due to this cause were but slight, and moreover were distributed over the whole curve traced out and included in the other general sources of error through the mode of observation of the different points adopted.

In order to obtain numerical values comparable with one another, it was necessary that each experiment should be made under as nearly as possible constant conditions (save as to time and temperature), especially as regards rate of hydrogen supply, quantity and physical condition of the metallic oxide, amount of surface exposed, &c., &c. Several hundred grams of oxide of copper were prepared from electrotype copper by solution in nitric acid, filtration, evaporation to dryness, and heating to redness in quantities of about 20 grams at a time in a well-covered platinum crucible, the ignition being finally completed over a gas blowpipe. Not until the whole series of experiments

* This Journal, 1876, **1**, p. 24.

was nearly completed was it found that this last operation might have introduced a complicating circumstance. At a temperature near a white heat an ordinary platinum crucible becomes sensibly pervious to reducing gases (probably hydrogen), so that if a mass of pulverulent copper oxide be heated over a gas blowpipe flame for half an hour or more that portion of the copper oxide in contact with the platinum becomes notably reduced, so much so as sometimes to be distinctly red and to give off copious red fumes on moistening (after cooling) with nitric acid. That this is not due to the infiltration of reducing gases from the lid of the crucible is shown by the circumstance that it takes place even if a perforated lid be employed, furnished with a tube delivering into the crucible a rapid current of air or carbon dioxide, whilst if a porcelain crucible be used instead of a platinum one, the reduction is practically stopped entirely, even though no stream of air or carbon dioxide be used. Fortunately in the preparation of the oxide of copper required for the curve determinations the ignition over the blowpipe was not carried on for more than a few minutes, so that the amount of reduction introduced was but slight; it was, however, appreciable, for the products of the several portions thus ignited, after pulverisation in a clean porcelain mortar, sifting through a very fine brass sieve and thoroughly intimate intermixture, gave the following numbers:—

1·2415 gram reduced with hydrogen at a red heat till constant lost 0·2455 gram.....		= 19·77 per cent.	
1·1540 „	lost 0·2275	= 19·71	„
1·1740 „	„ 0·2285	= 19·64	„
	Mean ..	19·71	„
Taking Cu = 63·5, calculated amount for CuO		20·12	„

whence a distinct deficiency in oxygen is noticeable. Moreover, on boiling with slightly acid ferric chloride, ferrous chloride was formed; on titration with permanganate numbers were obtained corresponding with those got by reduction in hydrogen, thus—

0·8570 gram required permanganate corresponding to 0·00417 oxygen	= 0·47 per cent.	
1·1135 gram required permanganate corresponding to 0·00524 oxygen	= 0·47	„
0·6190 gram required permanganate corresponding to 0·0031 oxygen	= 0·50	„
Mean	0·48	„

hence the percentage of oxygen originally present is 19·74, this being the value of x when $\frac{x + 0{\cdot}48}{100 + 0{\cdot}48} = \frac{20{\cdot}12}{100}$. These results correspond to the formula $Cu_{40}O_{39} = 38CuO, Cu_2O$.

	Found.	
Calculated for $Cu_{40}O_{39}$.	Mean from reduction in H.	Mean by titration.
19·72	19·71	19·74

The hydrogen employed was prepared from commercially pure granulated zinc and hydrochloric acid, being used direct from the generator after passing through **U**-tubes containing pumice stone soaked in caustic potash and silver nitrate. In order to obtain an equable stream of gas delivered as nearly as possible at a constant rate the gas was passed through a bubble arrangement consisting of a bottle half full of sulphuric acid and provided with a doubly perforated cork through which passed two glass tubes, one dipping under the sulphuric acid, one not doing so. By means of a Bunsen's screw clamp worked by a lever some inches long placed on a stout nonvulcanised india-rubber tube between the bubbler and the **U**-purifying tubes it was found tolerably easy to regulate the rate of bubbling of the gas through the acid to any required speed, 100 bubbles per minute being that finally adopted. In order to obtain anything like uniformity it was found indispensable to have no liquid potash or silver nitrate solution at the bottom of the **U**-tubes, and to have a tolerably constant back pressure of some ten inches of water in the hydrogen generator (consisting of two reservoirs united by an india-rubber tube between tubulations at their bases), easily obtained by elevating the acid reservoir on a stand. In order to determine how much hydrogen corresponded to a given rate of bubbling a number of preliminary experiments were needed. It was found that only rough results could be obtained by collecting the hydrogen delivered over water, because the bubbling up through the pneumatic trough affected the size of the bubbles in the bubbler, wherefore a gas-measuring arrangement was constructed on the principle of the gas reservoir of a gas-works, the bell being a graduated glass tube immersed in a wider tube, the bottom of which was closed by a doubly perforated cork, so that by turning suitable taps either water could be let into the cistern part of the arrangement from a reservoir at a higher level, or water could be run out, and thus the pressure in the bell kept almost exactly atmospheric, whether gas was allowed to enter it or to leave it. By means of this arrangement it was found that the size of the bubbles in the bubbler was not affected by small variations of pressure. Whether the water in the cistern stood an inch or two higher than that in the bell during

collection, an inch or two lower, or fluctuated, no perceptible difference was caused in the size of the bubbles; a marked alteration in their size, however, was produced by the interposition between the bubbler and the measuring arrangement of the narrow glass **U**-tubes containing copper oxide at the bend used in all the experiments. A considerable diminution in the size of the bubbles was thus caused, which diminution moreover was not constant, varying with the packing of the pulverulent copper oxide according as it was shaken down more or less. On an average it was found that 100 bubbles per minute, at a temperature of 15°, corresponded to a delivery of 16·14 c.c. at 15° and 760 m. per minute when no copper oxide **U**-tube was inserted, but that 16 per cent. less, or 13·5 c.c., were passed per 100 bubbles when the U-tube was inserted between the bubbler and collecting apparatus. When the copper oxide was very closely packed indeed the diminution rose to about 30 per cent., and when it was very loose (as when it was partially reduced in hydrogen and not shaken down) the diminution was as low as 5 per cent.; but, under the conditions obtaining in the majority of the experiments, it was close to 16 per cent.; so that the rate of delivery of gas was on an average very close to 13·5 c.c. at 15° and 760 m., or 12·5 c.c. normal = 0·00112 gram per minute. It is specially noticeable that the size of the bubbles was largely influenced by the rate at which they passed. Thus the following table gives the average results of a large number of accordant experiments from which a mean curve was deduced; in these the bubbler was directly connected with the measuring apparatus, no **U**-tube with copper oxide being between them:—

Time of passage of 100 bubbles.	c.c. of hydrogen at 15° and 760 m. per 100 bubbles.	Difference.
50 seconds	16·70	—
55 ,,	16·40	0·30
60 ,,	16·14	0·26
65 ,,	15·91	0·23
70 ,,	15·70	0·21
75 ,,	15·50	0·20
80 ,,	15·32	0·18
85 ,,	15·15	0·17
90 ,,	15·00	0·15
95 ,,	14·87	0·13
100 ,,	14·76	0·11
105 ,,	14·67	0·09
110 ,,	14·60	0·07
120 ,,	14·55	0·05
125 ,,	14·51	0·04
130 ,,	14·48	0·03
135 ,,	14·46	0·02
140 ,,	14·45	0·01

Similar results were obtained, as described in § 2, with carbon oxide.

The experiments were conducted as follows:—A number of precisely similar **U**-tubes were constructed of quill tubing, the bottoms being bent into regular semicircular curves of about $\frac{1}{4}$-inch radius, measured on the inner side of the curve; one end of the **U**-tube was bent over to a right angle, and slightly drawn out to admit of more easy connection by an india-rubber tube with the bubbler. A quantity of copper oxide was measured out in a platinum spoon fixed to a glass handle sufficient to just fill the semicircularly curved bottom of the **U**-tube; this was introduced by means of a small funnel (kept along with the spoon, under a shade to protect from dust). This quantity of oxide of copper averaged 1·15 gram, and was in every experiment very close to that weight (save in some observations made specially to test the influence of varying amounts of copper oxide). The quantity introduced was known by weighing the empty tube and the tube after introduction; or more simply, in view of the rest of the experiment, by weighing the tube filled with hydrogen, and covered with tightly fitting india-rubber caps beforehand, then introducing the oxide of copper, and filling again with hydrogen, and weighing again. The weighed **U**-tube being attached to the india-rubber tube connected with the bubbler, and the hydrogen stream regulated to the exact speed of 100 bubbles per minute, the **U**-tube was plunged into the vapour-bath, and the time noted. The vapour-bath in most of the experiments consisted of a copper bottle, into the mouth of which fitted a cork perforated with four holes, and cut in two by a vertical cut passing through two of them; these two halves of the cork embraced the two limbs of the **U**-tube, which just fitted into the two holes thus sliced asunder; the other two perforations (one in each half of the severed cork) served to insert a thermometer into the vapour-bath, and for the adaptation of a long tube to condense the vapour and act as a cohobator. This arrangement permitted of a rapid entrance or withdrawal of the **U**-tube from the vapour-bath, whilst yet enabling a tolerably vapour-tight cork junction to be made at the mouth of the copper bottle. When the required time of exposure had elapsed the **U**-tube was withdrawn, cooled down as quickly as possible with the hydrogen passing through it, and finally closed with the india-rubber caps and quickly weighed.

A correction was found to be necessary as to the time of exposure; some few seconds or more elapsed before the bend of the **U**-tube rose up to the temperature of the vapour-bath; an estimate as to this time was obtained by noticing how long it took a thermometer to rise to within a degree or two of its stationary temperature. On the other hand, the tube and contents did not cool down instantaneously below

the temperature at which reduction could take place on withdrawal from the bath; so that reduction was actually going on for a slightly longer period than that during which the **U**-tube was in the bath, after correction for the time taken to heat up the **U**-tube. An allowance of a few seconds more or less, according to the temperature, was made for this, the usual mode of combining both corrections being to note the time at which a thermometer introduced simultaneously with the **U**-tube reached to a point a few degrees below its stationary temperature, and to expose for the required time after this, removing the **U**-tube at the end of the time; it being considered that the deficiency in reduction, owing to the tube being not quite heated up on first taking the time, was about balanced by the slight amount of reduction going on during cooling after removal from the bath. It is true that a slight degree of uncertainty as to the true average times of exposure is unavoidable; but the error due to this cause is small compared with other sources of discrepancy.

One point essential to discover, first of all, was whether the hydrogen stream was thoroughly heated up to the temperature of the vapour-bath before coming in contact with the copper oxide. It was found that when the **U**-tube was of such length that 4 to 5 inches were inside the cork in the vapour, the hydrogen was perfectly brought to the temperature of the bath in passing through the heated upper part of the tube; this was shown by fixing two thermometers, one inside the vapour-bath, one inside the **U**-tube, containing no copper oxide, with the bulb as near the bend as possible. Series of readings of both thermometers were then taken, both when no hydrogen was passed, and when the usual current or a more rapid one was employed. On contrasting the average of a dozen readings of each thermometer it was found that precisely the same temperature difference was registered by the two thermometers in each case, which could not have been the case had the hydrogen been cooler than the vapour when it reached the thermometer inside the **U**-tube. Even with a hydrogen stream of double the normal rate (*i.e.*, double 12·5 c.c. per minute at 0° and 760), the gas was completely heated up to the temperature of the bath before reaching the bend.

An opposite kind of error to that which would have been occasioned by deficient heating up of the hydrogen is apt to be introduced by the circumstance that during reduction of copper oxide by hydrogen an evolution of heat takes place on the whole; and consequently when action has commenced, the temperature of the partially reduced copper oxide may rise above that of the bath owing to this development of heat. Such a rise is not likely to be great when the copper oxide is in a narrow tube, as the extra heat would be quickly carried off by conduction, and especially by the escaping hydrogen and steam. In

order to gain some information as to whether this development of heat was appreciable, readings were taken as above with two thermometers (one in the **U**-tube, one in the vapour-bath) firstly before any hydrogen current was turned on, nextly, whilst the average current of 12·5 c.c. normal was passing, the bend of the **U**-tube having been filled with copper oxide previously. In this way it was found in a vapour-bath of naphthalene that whilst the difference of scale-readings of the two thermometers was 2·35° (average of 20 readings of each thermometer), when no hydrogen current was passing, it was 2·44° (average of 10 readings) during the period when from 20 to 50 per cent. of the oxygen present was being removed from the copper oxide, and also 2·44° (average of 10 readings) during the periods when 50 to 80 per cent. was being removed. As shown below these periods correspond to the most rapid removal of oxygen, whilst the naphthalene bath temperature is almost the highest tried, again corresponding to most rapid deoxidation; even under these circumstances, however, the extra development of heat was only sufficient to heat the issuing hydrogen and steam up to 0·09° C. higher than the bath temperature. As shown in § 2 similar experiments with carbon oxide led to an analogous result; only in this case, as more heat is developed during reduction by carbon oxide than by hydrogen, the extra development of heat caused a greater difference between the two thermometers, not exceeding 0·25° however.

The **U**-tubes containing partially reduced oxide of copper were necessarily weighed as soon as possible, *i.e.*, as soon as they had cooled down to the temperature of the air. Under these conditions a tube of the size used (made from some 14 inches length of quill tubing) weighs less by some two milligrams than it would do if kept (in dry air) for an hour or two and then weighed, owing to the non-immediate re-absorption of the film of air condensed on its surface, and partially removed by heating.* In order to avoid this source of error

* Although the fact has been repeatedly pointed out that the weight of a recently heated vessel (*e.g.*, a crucible), weighed when just cold, is perceptibly less than its weight after standing an hour or two (even over sulphuric acid) owing to the slow recondensation on the surface of an air-film, yet as many experimenters seem to be unaware of the extent of the possible errors thus introduced, it may be as well to point out that the weight of an ordinary small Berlin porcelain covered crucible may differ 1, 2, or even 3 milligrams, according as it is weighed immediately after cooling, or after standing, so as again to take up the air-film. In organic analysis this point is of importance, as the heat radiated from the combustion furnace on to the potash bulbs will often expel sufficient air-film to make them weigh 1 or 2 milligrams less than their weight after standing an hour or two (of course with caps on). It is convenient to warm and then cool again the bulbs just before filling them with potash, and taking the first weighing: by this means the condition of the air-film before and a few minutes after the combustion is rendered practically the same.

the **U**-tube was always heated, and then cooled again before filling with hydrogen to take the weight of the empty tube, so that the condition of the air-film should be as nearly as possible the same at every weighing. A tube that had been used once was always carefully cleaned out with hot nitric acid before being used again, to avoid the possibility of particles of partially reduced substance adhering to it, and perchance causing, by contact action, reduction to commence earlier than it would otherwise have done.

The first experiments made led to the conclusion (borne out by subsequent results) that reduction of copper oxide by hydrogen does not always commence at once, but that in certain cases (*i.e.*, below a certain temperature) a certain amount of time must elapse before the action commences, and a yet longer time before it attains a constant rate, *i.e.*, before it ceases increasing in rate. The following experiments, however, lead to the curious result that in many cases, when the action has once started, allowing the substance to cool down and to stand for a sufficient length of time to take a weighing does not interfere noticeably with the rate of action on putting back again into the vapour-bath. This is not invariably the case, however, a distinct retardation being noticeable by interrupting the action when it takes place at temperatures below a certain limit, and even above this limit a retardation is still noticeable, if some hours elapse before the **U**-tube is put back again into the bath, *e.g.*, when an experiment is interrupted over night and resumed next morning. Accordingly the observations made may be grouped into two kinds, viz., those where the exposure was carried out for a given time without an interruption, and those where the exposure was interrupted once or more; these latter observations were obtained by simply replacing the **U**-tube in the bath after the first weighing for the uninterrupted observation had been made, and going on for a fresh period of exposure, and so on; at temperatures above 160° the uninterrupted observations and the interrupted ones do not differ from one another more than those of the first kind do amongst themselves, so that on taking a sufficiently large number of observations, the mean curve-values deduced from each set are practically identical. In other words, whether the oxide of copper be exposed for a time T at one operation, or for a series of times t_1, t_2, t_3, ... jointly equal to T, makes no material difference, provided firstly that the temperature is not below the limit of about 160°, and secondly, the intervals elapsing between the periods t_1 and t_2, t_2 and t_3, ... do not exceed some ten minutes or so.

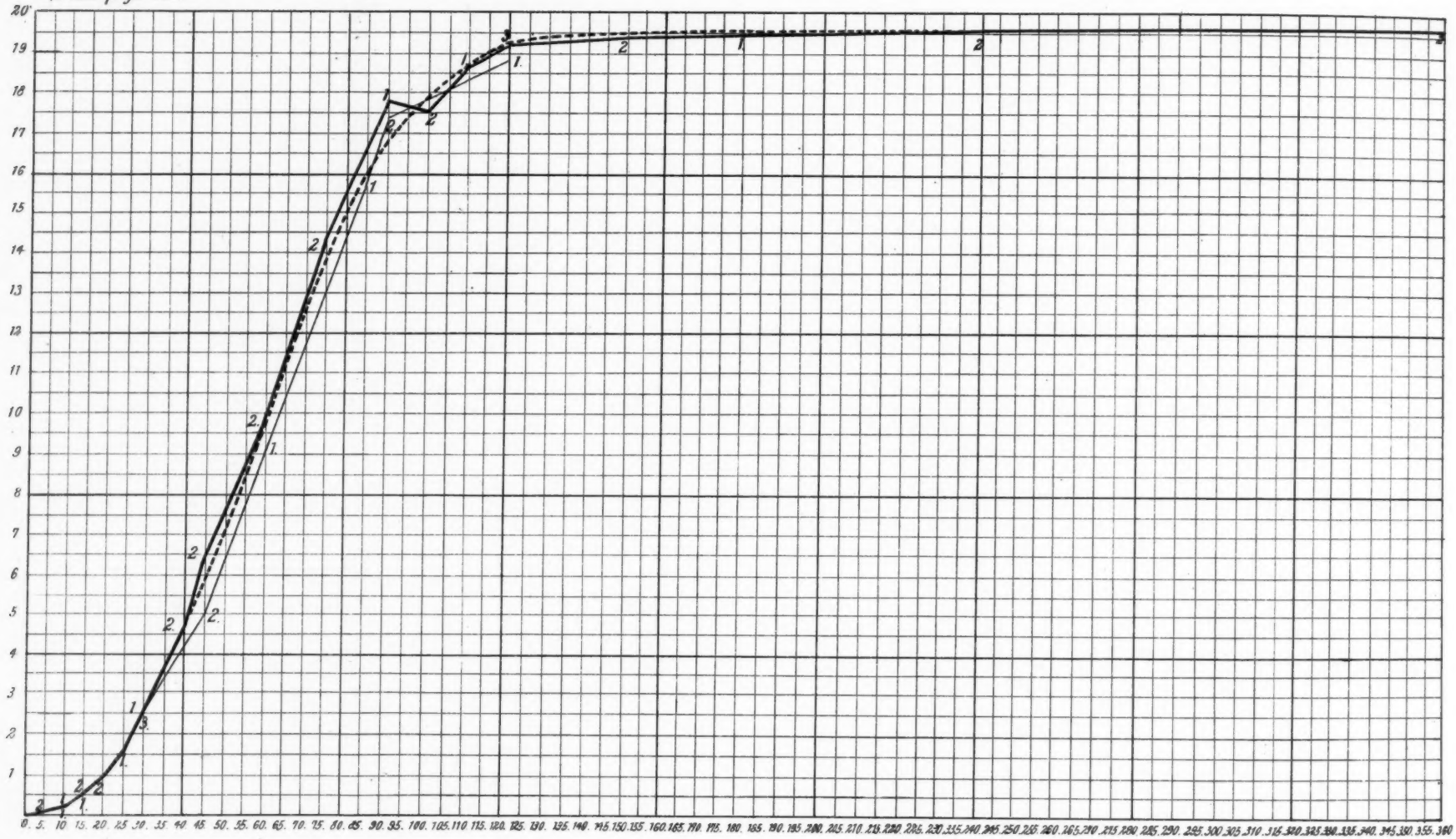
Thus the following numbers were obtained in a vapour-bath of aniline, the average corrected temperature throughout the series of

Obviously weighings to less than half a milligram are utterly superfluous in all such cases.

Time in minutes.	Percentage loss of oxygen.													Averages.	
														Uninterrupted observations.	Interrupted observations.
5	0·09	0·04	—	—	—	—	—	—	—	—	—	—	—	0·06	—
10	0·18	—	0·20	—	—	—	—	—	—	—	—	—	—	0·20	0·18
15	0·50	—	—	0·48	0·49	—	—	—	—	—	—	—	—	0·48	0·50
20	0·91	0·92	—	—	—	—	—	—	—	—	—	—	—	—	0·91
25	—	1·56	—	—	—	—	—	—	—	—	—	—	—	—	1·56
30	2·61	—	—	2·16	2·75	2·49	—	—	—	—	—	—	—	2·49	2·52
40	—	4·67	—	4·76	—	—	—	—	—	—	—	—	—	—	4·71
45	6·88	—	—	—	6·19	—	5·04	4·96	—	—	—	—	—	5·00	6·53
60	—	9·64	—	—	—	10·21	—	—	9·31	—	—	—	—	9·31	9·92
75	—	—	—	—	—	—	14·58	—	13·83	—	—	—	—	—	14·20
85	—	—	—	—	—	—	—	—	—	15·73	—	—	—	15·73	—
90	—	—	—	—	—	—	—	—	—	17·74	16·33	18·56	—	17·44	17·74
100	—	—	—	—	—	17·72	—	—	—	—	17·49	—	—	—	17·60
110	—	—	—	—	—	—	—	—	—	—	18·64	—	—	—	18·64
120	—	—	—	—	—	—	—	19·16	—	19·39	—	19·44	18·83	18·83	19·33
150	—	—	—	—	—	—	—	—	19·48	—	—	—	19·25	—	19·36
180	—	—	—	—	—	—	—	—	—	19·65	—	—	—	—	19·65
240	—	—	—	—	—	—	—	—	—	19·70	—	—	19·46	—	19·58
360	—	—	—	—	—	—	—	—	—	19·76	19·58	—	—	—	19·67

Fig 1.

To face page 485.



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observations being 184·5,° and the actual temperature at any given stage of any given experiment not being so much as 1° above or below the average, and generally within 0·25° of the average. The numbers represent the percentages of oxygen lost, the percentage originally present being 19·74 (*i.e.*, complete reduction equals a loss of 19·74 per cent.). The numbers placed in the same vertical column were all obtained with the same portion of oxide of copper, so that in each column the figure corresponding to the shortest time exposure is an "uninterrupted observation," and those corresponding to longer exposures are "interrupted observations," the period of interruption in each case being ten minutes or so, just enough to cool down thoroughly and weigh.

The annexed diagram (Fig. 1) represents these results, the thin line connecting the points deduced from uninterrupted observations, and the thick one those obtained from the interrupted observations; the numerals at the points represent the numbers of observations furnishing the points respectively as averages. It is evident from inspection of the curve, and of the preceding table giving the isolated observations themselves, that the mean curves deducible from the uninterrupted and interrupted observations are practically identical. The dotted line represents this mean curve, and the following table the average values thence reckoned.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	0·06	0·06	0·06	0·012
10	0·19	0·13	0·07	0·026
15	0·46	0·27	0·14	0·054
20	0·93	0·47	0·20	0·094
25	1·62	0·69	0·22	0·138
30	2·50	0·88	0·19	0·176
35	3·56	1·06	0·18	0·212
40	4·71	1·15	0·09	0·230
45	5·92	1·21	0·06	0·242
50	7·18	1·26	0·05	0·252
55	8·48	1·30	0·04	0·260
60	9·81	1·33	0·03	0·266
65	11·16	1·35	0·02	0·270
70	12·49	1·33	−0·02	0·266
75	13·76	1·27	−0·06	0·254
80	14·93	1·17	−0·10	0·234
85	15·95	1·02	−0·15	0·204
90	16·73	0·78	−0·24	0·156

University of Michigan

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
95	17·34	0·61	−0·17	0·122
100	17·84	0·50	−0·11	0·100
105	18·27	0·43	−0·07	0·086
110	18·65	0·38	−0·05	0·076
115	18·99	0·34	−0·04	0·068
120	19·30	0·31	−0·03	0·062
150	19·50	0·20	—	0·007
180	19·65	0·15	—	0·005

From the general sigmoid character of the curve, it is evident that the rate of reduction during the first five minutes is so small as to be practically inappreciable, and that it then gradually increases to a maximum, after which it gradually decreases until complete reduction is attained. It might be supposed that the apparent minute amount of action during the first few minutes is not real, but is simply due to the retention in the oxide of copper of all, or almost all, of the water formed by the reaction, thus preventing any large loss of weight from being noticed. That this is not so, however, was shown in two ways; firstly, on titrating with permanganate (after solution in ferric chloride) the copper oxide after various short exposures during which no large loss of weight had taken place, no greater amount of reduction could be detected than that indicated by loss of weight; and secondly, on heating the slightly reduced substances to redness in a current of pure dry nitrogen (evolved from potassium nitrite and ammonium chloride), a chloride of calcium tube being attached, neither loss in weight of the oxide of copper, nor gain in weight of the chloride of calcium tube could be detected, clearly showing that no water was retained by the oxide of copper. Whether the reduction took place at as low a temperature as 130°, or at higher temperatures, and whether 5, 50, or 99 per cent. of the oxygen present had been removed, this same negative result was found, viz., that no measurable amount of moisture was retained by the copper oxide. Out of many experiments, the details of which it is unnecessary to quote, only one indicated a weighable amount of moisture as being retained, and this single case was where 3·1 per cent. of loss of weight (out of 19·74 per cent. of the oxygen originally present) had been occasioned by heating for several hours at 130°; even in this solitary instance, however, the loss of weight of the copper oxide on ignition in nitrogen, and the gain in weight of the chloride of calcium tube were each only 0·5 milligram, a quantity hardly greater than the possible weighing errors through air-films, &c., and only corresponding to 0·04 per cent. on the weight of oxide of copper

employed (1·150 gram). In no other experiment was either the loss of the one or the gain of the other greater than 0·25 milligram, *i.e.*, greater than the possible weighing error.

It may be noticed in this connection, that the spongy copper obtained after 3—4 hours' heating to 184·5°, and that produced at somewhat higher temperatures in shorter periods (*e.g.*, 50—60 minutes at 256°), was so nearly perfectly reduced, that on further heating to redness in hydrogen, it only lost 0·1 to 0·2 per cent. in weight; reduction to such a stage that no further loss occurred on heating to redness in hydrogen was, however, never brought about, even after 6—8 hours' heating at 184·5, or a little higher. Of the small quantity of weight further lost at a red heat, doubtless a portion was due to occluded hydrogen; the quantity of hydrogen obtained as such on Sprengel-pumping at a red heat from a gram or two of this copper was however so minute as to be wholly immeasurable, less than 0·1 c.c. of total gas being obtained, and this apparently consisting only of air. According to Graham (*Trans. Roy. Soc.*, 1866, 432), and Thudichum and Hake (this Journal, 1876, ii, 251), from 0·01 to 0·08 c.c. of hydrogen are obtainable per gram of compact metallic copper reduced on the surface by hydrogen after superficial oxidation (as in the preparation of copper for organic analysis). Since, however, quantities of *water*, corresponding to considerably larger amounts of hydrogen, have been shown by Melsens (*Ann. Chim. Phys.*, 1843, [iii], **8**, 205); Lietzenmayer (*Deut. Chem. Ges. Ber.*, 1878, 306); and Johnson (this Journal, 1876 [i], 178, and 1879 [i], 243), to be formed by heating such reduced copper in dry air, it seems highly probable that the non-withdrawal of hydrogen in more than minute quantity by Sprengel-pumping at a red heat is due, not to the hydrogen not being there, but to its acting on the small quantity of unreduced copper oxide present (probably disseminated through the mass of metal), and consequently escaping as water. In just the same way, if iron oxide be almost but not quite completely reduced at a bright red heat by carbon oxide, and cooled down in a current of that gas, a spongy metal containing occluded carbon oxide will be obtained; on Sprengel-pumping this, however, and gradually heating, much carbon dioxide is pumped out, as well as carbon oxide, the former being doubtless formed by the reaction of the latter on the small quantity of iron oxide still present; just as in the experiments described in Parts I and II, on the reduction of metallic oxides by free carbon, the gas pumped out on Sprengelising the mixture, and heating till reduction commenced, consisted usually of little save carbon dioxide, the carbon monoxide presumably first formed being instantly further oxidised by the metallic oxide present.

It would naturally be expected that at temperatures higher than 184·5°, the rate of reduction would be more rapid than that observed

at this temperature; in order to see if analogous sigmoid curves represent the character of the action at higher temperatures, the above experiments were repeated twice, using in the first case a vapour-bath of naphthalene, to which a little of a high boiling fluid distillate from citronella oil had been added, to make the volatilised portion sufficiently fusible to avoid all risk of choking up the condensing tube by deposition of solid naphthalene; and in the second instance the hydrocarbon of cubeb oil separated by fractional distillation. The average vapour temperatures in these two cases were respectively 210° (corrected) and 256·5° (corrected), the actual temperature differing but little from these numbers in every observation. The following values were obtained:—

Time in minutes.	At 210°. Percentage loss of oxygen.									Averages.	
										Uninterrupted.	Interrupted.
5	0·12	—	—	—	—	—	—	—	—	0·12	—
10	—	0·58	0·73	—	—	—	—	—	—	0·65	—
15	1·34	—	1·81	1·39	—	—	—	—	—	1·39	1·57
20	—	—	3·28	—	2·60	—	—	—	—	2·60	3·28
25	—	5·28	4·94	—	—	3·86	—	—	—	3·86	5·11
30	6·04	—	—	6·78	—	—	6·46	—	—	6·46	6·41
40	—	12·05	—	—	—	—	—	12·88	—	12·88	12·05
45	14·09	—	—	13·96	—	—	12·04	—	—	—	13·36
50	—	—	—	—	—	—	—	—	14·50	14·50	—
55	—	—	—	17·45	—	—	15·83	—	—	—	16·61
60	—	—	—	—	—	—	—	—	17·63	—	17·63
65	—	—	—	19·28	—	—	—	—	18·59	—	18·93
70	—	19·50	—	—	—	—	—	—	—	—	19·50

Time in minutes.	At 256·5°. Percentage loss of oxygen.									Averages.	
										Uninterrupted.	Interrupted.
3	0·60	—	—	—	—	—	—	—	—	0·60	—
3½	—	0·77	—	—	—	—	—	—	—	0·77	—
5	—	—	1·12	—	—	—	—	—	—	1·12	—
8	3·71	—	—	—	—	—	—	—	—	—	3·71
10	—	4·09	—	4·84	3·41	—	—	—	—	4·12	4·09
15	—	—	7·75	—	—	5·85	—	—	—	5·85	7·75
20	—	11·00	—	10·55	—	—	10·40	—	—	10·40	10·77
25	—	—	13·96	—	—	11·70	13·89	13·42	—	13·42	13·18
30	—	17·13	16·98	17·04	—	15·74	—	—	16·96	16·96	16·72
35	—	19·16	—	—	—	18·32	18·56	—	—	—	18·68
40	—	—	—	—	—	—	—	18·94	19·34	—	19·14
45	—	—	—	—	19·61	—	—	—	—	—	19·61

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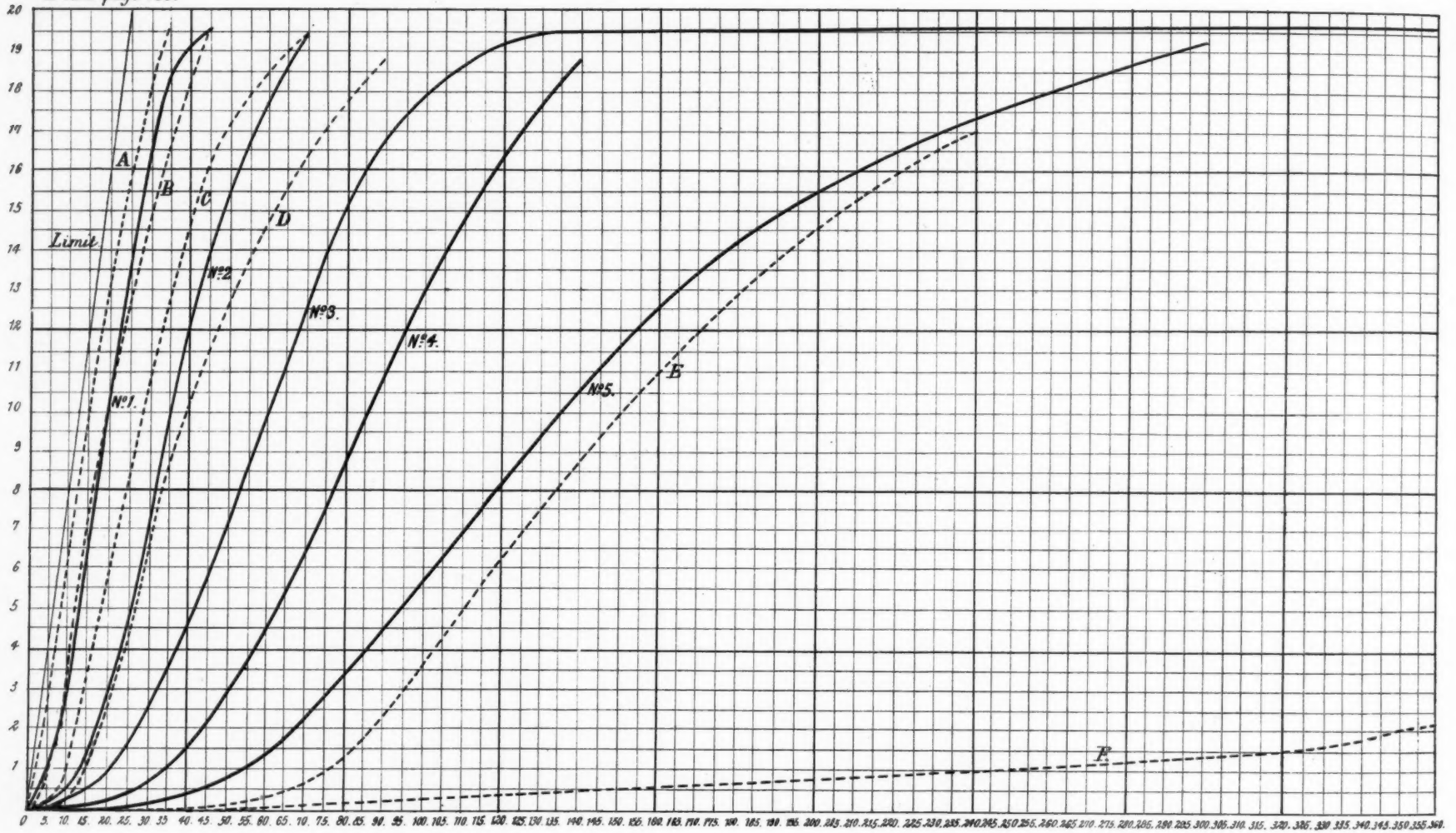
Fig. 2.

To face page 489.



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Curves Nos. 1 and 2 (thick continuous lines) in the diagram (Fig. 2) represent these average results, the curve marked No. 3 being the corresponding mean curve obtained at 184·5°. The straight sloping line to the left marked "limit" indicates the limit to which the curves all tend, this being the line that would be traced out did deoxidation commence at the first instant and go on at such a rate that every trace of hydrogen was converted into steam. To reduce 1·15 gram of copper oxide containing 19·74 per cent. of oxygen would require 24·2 minutes' passage of a stream of hydrogen conveying 12·5 c.c. of hydrogen (at 0° and 760 m.) per minute.

The following values are deduced from these average curves:—

Time in minutes.	Percentage loss.	At 210°. Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	0·10	0·10	0·10	0·020
10	0·50	0·40	0·30	0·080
15	1·35	0·85	0·45	0·170
20	2·80	1·45	0·60	0·290
25	4·70	1·90	0·45	0·380
30	6·95	2·25	0·35	0·450
35	9·40	2·45	0·20	0·490
40	11·85	2·45	0	0·490
45	14·00	2·15	−0·30	0·430
50	15·55	1·55	−0·60	0·310
55	16·70	1·15	−0·40	0·230
60	17·65	0·95	−0·20	0·190
65	18·57	0·92	−0·03	0·184
70	19·49	0·92	−0	0·184

Time in minutes.	Percentage loss.	At 256·5°. Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	1·10	1·10	1·10	0·22
10	3·80	2·70	1·60	0·54
15	6·95	3·15	1·45	0·63
20	10·45	3·50	0·35	0·70
25	13·70	3·25	−0·25	0·65
30	16·50	2·80	−0·45	0·56
35	18·50	2·00	−0·80	0·40
40	19·20	0·70	−1·30	0·14
45	19·60	0·40	−0·30	0·08

Evidently the curves for 184·5°, 210°, and 256·5°, are all of the same general character; before drawing deductions from them, the results obtained at temperatures below 184·5° must be considered. In order to obtain them experiments similar to the preceding ones were carried out in vapour-baths giving lower temperatures, viz., in cajeputol vapour giving an average temperature of 175° (corrected); hydrocarbon from oil of turpentine, 160° (corrected); a petroleum distillate, 150° (corrected); fusel oil, 130° (corrected); glacial acetic acid, 118° (corrected); and water, 100°; the first four of these substances were subjected to several fractional distillations before use, so as to obtain substances of as nearly as possible constant boiling points.

One point in connection with these values is noteworthy; whereas at 184·5° and upwards, the values obtained never showed any very marked discrepancy or inconsistency, but always approached reasonably close to a mean value; it occasionally happened at temperatures lower than 184·5° that irregularities were observed of this kind, that whilst the majority of the observations agreed fairly together, giving a mean value the probable error of which was but small, now and then the copper oxide was not acted upon at all for a considerably longer period than that observed in the other cases, and consequently gave, when action did at length commence, numbers not agreeing with the mean curve deduced from the accordant observations, but close to a curve parallel with this mean curve, and lying to its right hand, as the curves are drawn in the diagram; in other words, an abnormal prolongation of the period during which the action was so slight as to be imperceptible was noticed in some few instances. At 175° and 160° these irregular observations were comparatively rare; but below 160° they were so frequent as to prevent any concordance at all between the results.

The following values were obtained in nine accordant experiments at 175°:—

Time in minutes.	Percentage loss of oxygen.									Averages.	
										Uninterrupted.	Interrupted.
10	0	—	—	—	—	—	—	—	—	0	—
15	—	0·07	0·12	—	—	—	—	—	—	0·09	—
20	0·27	—	—	—	—	—	—	—	—	—	0·27
25	—	0·31	—	—	—	—	—	—	—	—	0·31
30	0·54	—	0·73	0·82	—	—	—	—	—	0·82	0·63
35	—	0·75	—	—	1·65	0·86	—	—	—	1·25	0·75
40	—	—	—	—	2·37	—	—	—	—	—	2·37
45	1·59	—	2·15	—	3·33	—	1·75	—	—	1·75	2·36
60	3·92	—	—	5·11	5·55	—	—	4·94	—	4·94	4·86
65	—	—	—	—	—	5·32	—	—	—	—	5·32
75	7·11	—	7·85	—	8·11	—	7·40	—	—	—	7·62
80	—	—	—	—	9·01	—	—	—	—	—	9·01
90	10·14	—	—	—	—	—	10·35	9·88	11·64	11·64	10·12
95	—	—	11·64	—	—	—	—	—	—	—	11·64
105	—	—	—	—	—	—	—	12·47	14·32	—	13·39
120	—	—	—	—	—	—	16·24	15·37	17·04	—	16·22
140	—	—	—	—	—	—	18·87	—	—	—	18·87

In two other observations a marked retardation was noticed; in one at the end of 60 minutes the loss was only 0·43 per cent. instead of 4·51 per cent., as indicated by the mean curve deduced from the preceding nine experiments; in the other the losses at 50, 55, and 60 minutes respectively were 0·21, 0·34, and 0·61 per cent., instead of 2·79, 3·61, and 4·51, as indicated by the mean curve.

Rejecting these two abnormal results, the above figures yield a mean curve, which is traced on the diagram, and marked No. 4. From this the following values are obtained:—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
0	0	0	0	0
5	0	0	0	0
10	0	0	0	0
15	0·06	0·06	0·06	0·012
20	0·18	0·12	0·06	0·024
25	0·37	0·19	0·07	0·038
30	0·64	0·27	0·08	0·054
35	1·00	0·36	0·09	0·072
40	1·47	0·47	0·11	0·094
45	2·07	0·60	0·13	0·120
50	2·79	0·72	0·12	0·144
55	3·61	0·82	0·10	0·164

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 5 minutes.
60	4·51	0·90	0·08	0·180
65	5·47	0·96	0·06	0·192
70	6·48	1·01	0·05	0·202
75	7·53	1·05	0·04	0·210
80	8·61	1·08	0·03	0·216
85	9·71	1·10	0·02	0·220
90	10·81	1·10	0	0·220
95	11·89	1·08	−0·02	0·216
100	12·93	1·04	−0·04	0·208
105	13·90	0·97	−0·07	0·194
110	14·78	0·88	−0·09	0·176
115	15·58	0·80	−0·08	0·160
120	16·32	0·74	−0·06	0·148
125	17·01	0·69	−0·05	0·138
130	17·66	0·65	−0·04	0·130
135	18·28	0·62	−0·03	0·124
140	18·88	0·60	−0·02	0·120

Five observations at 160° gave the following accordant results:—

Time in minutes.	Percentage loss of oxygen.					Averages.	
						Uninterrupted.	Interrupted.
20	0	—	—	—	—	0	—
30	—	0·08	—	—	—	0·08	—
40	0·29	—	—	—	—	—	0·29
50	—	0·69	—	—	—	—	0·69
60	1·06	—	1·25	—	—	1·25	1·06
90	3·93	4·58	5·02	—	—	—	4·51
120	7·69	—	8·36	—	—	—	8·02
150	10·95	12·89	11·39	10·93	—	10·93	11·74
180	14·28	—	13·20	14·15	—	—	13·88
210	—	16·69	15·28	16·75	17·01	17·01	16·23
240	—	—	17·32	—	—	—	17·32
270	—	—	18·66	—	—	—	18·66
300	—	—	19·22	—	—	—	19·22

Another experiment, however, furnished numbers indicating a considerable retardation in the commencement of the action; in 60, 90, and 150 minutes the losses were respectively 0·18, 1·83, and 7·39 per cent., or close to those representing a curve parallel to that deduced from the above five experiments, but shifted to the right

through a space representing about 30 minutes. Neglecting this abnormal experiment the above numbers furnish the mean curve marked No. 5 in the diagram, from which the following figures are deduced :—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute during each consecutive 30 minutes.
20	0	—	—	—
30	0·08	0·08	0·08	0·003
40	0·28	—	—	—
50	0·64	—	—	—
60	1·20	1·12	1·04	0·037
90	4·50	3·30	2·18	0·110
120	8·05	3·55	0·25	0·118
150	11·60	3·55	0	0·118
180	14·15	2·55	−1·00	0·085
210	16·00	1·85	−0·70	0·062
240	17·30	1·30	−0·55	0·043
270	18·35	1·05	−0·25	0·035
300	19·30	0·95	−0·10	0·032

At temperatures below 160° the length of time which elapsed before any perceptible amount of reduction took place was much greater than the corresponding periods observed at 160° and upwards; and, moreover, on repeating observations considerable irregularities and discrepancies were noticed, so that it was impossible to obtain any numbers concordant enough to allow of a mean curve being deduced. Thus at 150° (in a bath of a petroleum distillate separated by repeated fractional distillation) the following numbers were obtained in four experiments :—

Time in minutes.	Percentage loss of oxygen.			
20	0	—	—	—
40	0	—	—	—
60	0	0·42	—	—
90	—	—	0	—
120	0	4·38	—	—
180	0·08	9·88	—	0·26
240	—	15·48	—	—
300	—	18·57	—	—

The second of these experiments, yielding by far the highest numbers, corresponds to a curve lying considerably below No. 5 (that obtained at 160°).

Similarly the following numbers were obtained in four experiments at 130° (in a fusel oil vapour-bath):—

Time in minutes.	Percentage loss of oxygen.			
60	0	—	—	—
180	0·17	0·13	—	—
240	—	—	0·26	—
270	1·71	—	—	—
360	3·48	0·26	—	0·43

The first of these experiments corresponds to a curve lying far below all the curves obtained at higher temperatures. In none of several experiments at 118° (glacial acetic acid) and 100° (water) was any reduction noticeable even after seven hours' uninterrupted exposure, *i.e.*, the period during which no action is perceptible exceeds seven hours at these temperatures.

No doubt the discrepant results occasionally observed as above described at 160° and 175°, and nearly always found at somewhat lower temperatures, arise from alteration in the physical texture of the copper oxide produced by continued exposure to heat during the period before any perceptible amount of action is noticed; as an illustration of the effect thereby produced in delaying the action the following figures are instructive. In three experiments made at 184·5° the copper oxide was heated just before use to a temperature short of redness in a porcelain crucible over a rose Bunsen burner, and weighed into the **U**-tube immediately after cooling, the rest of the experiments being performed precisely as before. In one of these three instances the numbers obtained approximated tolerably closely to the mean curve values above stated; in the second case a distinct retardation in the action was noticeable, and in the third case a very marked retardation was produced.

Time in minutes.	Percentage loss of oxygen.			Value from mean curve.
30	1·71	1·32	—	2·50
60	7·26	6·27	0·78	9·81
90	17·74	—	5·58	16·73
120	19·39	16·20	8·12	19·30
180	—	19·23	—	19·65

In two other experiments the copper oxide was heated in the **U**-tube in a current of air for some 15 minutes to 184·5°; the air current was then shut off, and the hydrogen current substituted, when the following numbers were obtained, clearly showing that the physical state of the copper oxide was materially influenced by the

previous heating in the current of air, a very marked retardation being produced in each case:—

Time in minutes.	Percentage loss of oxygen.		Value from mean curve.
5	0	—	0·06
10	0	—	0·19
15	0·05	—	0·46
20	0·11	—	0·93
30	0·16	0·05	2·50
60	—	0·20	9·81
120	—	5·83	19·30
180	—	15·60	19·65

Similarly, a portion of the copper oxide heated to below redness just before use, and then exposed at 160° as before, gave the following results:—

Time in minutes.	Percentage loss of oxygen.	Value from curve.
180	0	14·15
360	0·17	19·65
		Complete reduction.

indicating a very great amount of retardation.

On comparing together the five mean curves deduced as above described for the temperatures 256·5, 210, 184·5, 175 and 160° respectively, some noteworthy conclusions are deducible.

(1.) In all five cases for a length of time which is the shorter the higher the temperature, the action is so slight as to be almost or quite imperceptible, after which it goes on at an accelerating rate until a maximum rate is attained, when it again diminishes, owing doubtless to the admixture of reduced copper with the unaltered copper oxide; *i.e.*, the curves exhibit points of contrary flexure. In each case the point of contrary flexure corresponds to the removal of about half of the oxygen originally present. This non-instantaneous development of maximum action is the more marked the lower the temperature, being more particularly observable at 160° and lower temperatures still; it is evidently a case of the "chemical induction" studied by Bunsen and Roscoe (*Phil. Trans.*, 1857) in the case of the action of bromine water on tartaric acid, and the analogous "photochemical induction" observed when light acts on a mixture of chlorine and hydrogen.

(2.) The rates of increase in rate of action during the lower parts of the curve, and those of increase in rate of retardation during the latter halves, are not uniform throughout; during the lower halves whilst the rate of action increases continually, the increment in the

rate first increases from 0° to a maximum, and then decreases again to zero, when the point of contrary flexure is arrived at. Similarly, during the latter halves, the decrement in the rate of action increases in magnitude from 0 at the point of contrary flexure to a maximum, and then again decreases to 0 when complete reduction is arrived at. These variations are evident from the inspection of the columns headed "2nd Difference" in the mean curve tables given above. This may be otherwise put thus: the radius of curvature is at first infinite, and then decreases to a minimum, after which it again increases to infinity at the point of contrary flexure; it then changes its sign, decreases to a minimum of opposite sign to that of the first minimum, and finally again increases to infinity when perfect reduction is accomplished.

(3.) Between the commencement of the action and its end no sudden abrupt alteration in curvature is noticeable; especially no marked sudden alteration in curvature is noticeable when half the oxygen is removed, corresponding to the formation of Cu_2O; save that this point lies near to the point of contrary flexure, as might be expected, since after reduction to Cu_2O further reduction would produce metallic copper, which by partially covering up the unaltered oxide would tend to diminish the rate of action.

(4.) Whilst the duration of the period during which no action is perceptible is, as above stated, shorter the higher the temperature, the rates of increase in the rate of action during the first half and of decrease in rate of action during the second half, are greater the higher the temperature, as is also the maximum rate of reduction arrived at: the values of the maximum rates of reduction are:—

At 160°	0·118	per cent. of oxygen per minute (out of 19·74 per cent. originally present).	
„ 175	0·220	„	„
„ 184·5	0·270	„	„
„ 210	0·490	„	„
„ 256·5	0·700	„	„
Maximum possible	0·779	„	„

It is evident that the method above described for obtaining these curves is attended with a certain amount of experimental error, and that in consequence the mean curves deduced cannot be regarded as more than fair approximations. The chief sources of error are the uncertainty in the exact amount of hydrogen delivered by 100 bubbles, even when these pass exactly in the minute, and the chances of difference in amount of action from differences in the packing of the powdered oxide in the bend of the **U**-tube; whilst these errors are of such a kind as to be largely capable of elimination by taking a

numerous series of observations and averaging, they are yet sufficiently great to render it desirable to obtain, if possible, another check on the curve values. Accordingly a number of experiments were made with the object of directly checking these values by determining the ratio between the volume of hydrogen actually converted into steam, and that escaping unchanged at different periods of the reduction. Since the amount of copper oxide used in each experiment averaged 1·150 gram, and the average rate of supply of hydrogen was 12·5 c.c. normal = 0·00112 gram per minute, the average percentage of oxygen which could have been removed per minute by perfect conversion of the whole of the hydrogen into steam was $\frac{0{\cdot}00112 \times 8}{1{\cdot}150} \times 100 = 0{\cdot}7791$. Hence if x be the percentage of oxygen removed per minute at any period of the action, $\frac{x}{0{\cdot}7791}$ will be the fraction representing the ratio of the hydrogen oxidised to steam to the total amount employed, *i.e.*, the quantity of hydrogen employed being 100, the amount oxidised will be $\frac{x}{0{\cdot}7791} \times 100 = 128{\cdot}3 \times x$.

Thus, at the periods when the maximum rates of action were attained, the amounts of hydrogen oxidised were respectively—

At 160	$128{\cdot}3 \times 0{\cdot}118 = 15{\cdot}1$	per 100 of hydrogen employed.
„ 175	$128{\cdot}3 \times 0{\cdot}220 = 28{\cdot}2$	„ „
„ 184·5	$128{\cdot}3 \times 0{\cdot}270 = 34{\cdot}6$	„ „
„ 210	$128{\cdot}3 \times 0{\cdot}490 = 62{\cdot}8$	„ „
„ 256·5	$128{\cdot}3 \times 0{\cdot}700 = 89{\cdot}8$	„ „

In order therefore to obtain a check on the values of x deducible from the above mean curves, it is only required to determine the diminution in the bulk of a given quantity of hydrogen passed through the **U**-tube at the normal rate for a given time. By determining the amount of oxygen removed from the copper oxide at the beginning and end of the experiment, and taking the mean of the two amounts, a tolerably close approximation is obtained to the point on the curve corresponding to the mean value of x during the experiment, especially when the amounts of oxygen removed before and after the observation do not differ very largely.

The first experiments in this direction were made by passing hydrogen through the **U**-tube from one graduated vessel to another, so as to determine directly the diminution in volume brought about during the action; the results, however, were not at all sharp, owing to the great difficulty in making the current of gas pass regularly at anything approaching to the normal rate of 12·5 c.c. per minute. The following numbers obtained at 210°, with currents not far removed from the

normal one, however, approximate sufficiently to those calculated from the values of x deduced from the mean curve for 210° to bear out the general correctness of the character of the curve as regards its shape:—

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of hydrogen oxidised to H_2O.	
		Observed.	Calculated from formula $128{\cdot}3 \times x$.
6·0	0·42	47·1	53·9
8·2	0·47	57·8	60·3
9·0	0·48	67·9	61·6
9·6	0·49	55·4	62·8
13·0	0·46	50·5	59·0
14·45	0·40	44·5	51·3
15·05	0·35	35·1	44·9
16·5	0·25	32·9	32·1

Much better results were obtained by operating in the way by which the data for the mean curve values were obtained, and collecting the hydrogen that escaped at the far end in the gas works reservoir-like apparatus above described; the quantity of hydrogen converted into water was known by calculation from the loss of weight of the copper oxide during the experiment; adding this to the quantity collected at the far end, the total amount employed was known. Thus for instance, in one experiment at 256·5° the following data were obtained: 1·164 gram of copper oxide exposed in the **U**-tube for 12 minutes lost 0·061 gram = 5·24 per cent.: on further exposure for 8 minutes more, it further lost 0·067 gram = 5·75 per cent., making a total loss of 10·99 per cent. During this 8 minutes, the gas not oxidised collected at the far end amounted to 18·0 c.c. normal: whilst 0·067 gram of oxygen represents 0·008375 gram hydrogen = 93·8 c.c. normal. Hence 93·8 + 18·0 c.c. = 111·8 c.c. were passed in 8 minutes, or 13·97 c.c. per minute; and of this $\frac{93{\cdot}8}{111{\cdot}8} = 83{\cdot}9$ per cent. was oxidised to water. The loss of oxygen at the commencement of this observation being 5·24 per cent., and that at the end 10·99, the mean loss may be taken as 8·12 per cent.; the value of x corresponding to this, obtained by interpolation from the numbers in the table given above for the mean curve for 256·5°, is 0·652: whence $128{\cdot}3 \times 0{\cdot}652 = 83{\cdot}6$, the calculated percentage from the mean curve, agreeing with the number just found, 83·9 per cent., more closely than might have been anticipated, especially as the hydrogen current was somewhat more rapid than the normal one, viz., 13·97 c.c. per minute, instead of 12·5 c.c. In a similar way the following numbers were obtained in other experiments:—

At 256·5°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of hydrogen oxidised to H_2O. Observed.	Calculated from formula $128·3 \times x$.
3·0	0·46	61·4	59·0
4·4	0·57	74·3	73·1
8·1	0·65	83·9	83·4
10·8	0·70	88·5	89·8
13·7	0·65	80·8	83·4
17·75	0·46	59·4	59·0
	At 210°.		
1·5	0·19	25·6	24·4
3·5	0·31	40·9	39·8
8·2	0·47	59·8	60·3
9·5	0·49	62·4	62·8
11·7	0·49	62·3	62·8
18·3	0·19	25·5	24·4
	At 175°.		
0·27	0·031	2·7	3·9
0·47	0·043	5·6	5·5
2·0	0·117	13·0	15·0
2·9	0·147	18·3	18·9
6·6	0·202	21·4	25·9
8·4	0·215	29·4	27·6
9·9	0·220	29·6	28·2
12·1	0·215	28·7	27·6
16·0	0·152	24·6	19·5

The observed percentages of hydrogen oxidised to water, and those calculated from the mean curve values agree quite as closely as could be expected, considering the difficulty of keeping up an equable hydrogen current whilst the action was going on, and the unaltered gas was being collected at the far end. As a general rule, when the observed percentage falls below that calculated, the hydrogen current was a little more rapid than the normal one of 12·5 c.c. per minute, and *vice versâ;* as might be expected, *à priori*, since with the slower current the hydrogen was relatively a longer time in contact with copper oxide, and therefore was presumably more completely oxidised, and *vice versâ* with the more rapid current. In none of the above experiments, however, was the hydrogen current very different from the normal one.

That a hydrogen current more rapid than the normal one causes

absolutely a larger amount of reduction of copper oxide in a given time (although the amount of hydrogen oxidised is less relatively to the total amount employed), is shown by the following numbers obtained at 184·5° with a stream of nearly double the normal current, the other conditions being the same as before.

Time in minutes.	Percentage loss with rapid current.	Loss with normal current deduced from the mean curve.
20	2·08	0·93
40	13·22	4·71

Lessening the weight of copper oxide employed might be expected to produce the same result as increasing the speed of the hydrogen current; the following figures obtained at 184·5° show that this is the case, the increase in rate of reduction being greater the smaller the weight of copper oxide used; the hydrogen current in all these cases was the normal one.

Weight of copper oxide used in grams.	0·992	0·972	0·929	0·9215	0·8525	0·8245	Values deduced from mean curve.
Percentage loss after							
20 minutes	—	1·90	1·88	—	2·17	2·42	0·93
30 „	—	5·67	4·84	—	—	—	2·50
35 „	6·14	—	—	—	7·68	—	3·56
40 „	—	—	—	6·18	—	9·33	4·71
45 „	—	—	10·76	—	—	—	5·92
75 „	—	—	—	17·68	—	—	13·76
85 „	—	—	—	19·15	—	—	15·95

Conversely, the opposite effect was produced to some extent by increasing considerably the weight of copper oxide employed: thus with 1·7645 gram of copper oxide the following numbers were obtained at 184·5° with a normal hydrogen current:—

		Values from mean curve (obtained with 1·15 gram).
Percentage loss after 20 minutes..	0·73	0·93
„ „ 40 „ ..	3·74	4·71

When the above five mean curves are employed to generate a surface as described in the earliest portion of this report, and sections of this surface are made so as to generate the two other classes of curves there described (viz., those illustrating the connections between the amounts of deoxidation produced in a given time at various temperatures, and those indicating the relations between the times and tem-

peratures required to produce a given amount of deoxidation), the following numbers are obtained:—

Amounts of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	Temperatures.				
	160°.	175°.	184·5°.	210°.	256·5°.
5	0	0	0·06	0·10	1·10
10	0	0	0·19	0·50	3·80
15	0	0·06	0·46	1·35	6·95
20	0	0·18	0·93	2·80	10·45
25	0·03	0·37	1·62	4·70	13·70
30	0·08	0·64	2·50	6·95	16·50
35	0·16	1·00	3·56	9·40	18·50
40	0·28	1·47	4·71	11·85	19·20
45	0·44	2·07	5·92	14·00	19·60
50	0·64	2·79	7·18	15·55	—
55	0·89	3·61	8·48	16·70	—
60	1·20	4·51	9·81	17·65	—
65	1·61	5·47	11·16	18·57	—
70	2·15	6·48	12·49	19·49	—
75	2·73	7·53	13·76	—	—
80	3·32	8·61	14·93	—	—
85	3·91	9·71	15·95	—	—
90	4·50	10·81	16·73	—	—
95	5·09	11·89	17·34	—	—
100	5·68	12·93	17·84	—	—
105	6·27	13·90	18·27	—	—
110	6·86	14·78	18·65	—	—
115	7·45	15·58	18·99	—	—
120	8·05	16·32	19·30	—	—
125	8·64	17·01	—	—	—
130	9·23	17·66	—	—	—
135	9·82	18·28	—	—	—
140	10·41	18·88	—	—	—
150	11·60	—	—	—	—
180	14·15	—	—	—	—
210	16·00	—	—	—	—
240	17·30	—	—	—	—
270	18·35	—	—	—	—
300	19·30	—	—	—	—

Lengths of Time in Minutes required to produce given Amounts of Deoxidation at different Temperatures.

Percentages of oxygen removed (19·74 per cent. originally present).	Times.				
	At 160°.	At 175°.	At 184·5°.	At 210°.	At 256·5°.
1	57	35	20	13	5
2	67	44	27	17	7
3	77	51	32	20	9
4	86	57	37	23	11
5	95	62	41	26	13
6	103	67	45	28	14
7	111	72	49	30	15
8	120	77	53	32	17
9	128	82	57	34	18
10	136	86	60	36	19
11	145	90	64	38	21
12	155	95	68	40	22
13	166	100	72	42	24
14	178	106	76	45	26
15	193	112	80	48	27
16	210	118	85	52	29
17	233	125	92	57	31
18	260	133	102	62	34
19	291	142	115	67	39

§ 2. *Determination of Relations existing between Rate of Reduction of Copper Oxide by Carbon Oxide, Time, and Temperature.*

The results above described show that the particular temperature at which the action of hydrogen on copper oxide (prepared by calcining the nitrate) is first perceptible, depends to a notable extent on the length of time allowed for the observation with the particular sample employed; for example, if ten minutes be taken as the time of observation, the "temperature of initial action" deducible from the preceding observations would be about 180°, since no loss of weight was experienced at 175° in ten minutes, whilst 0·19 per cent. was lost at 184·5°: if, however, fifteen minutes were allowed for the observation, the "temperature of initial action" would be taken as about 167°, since a slight loss was experienced during that time at 175°, but none at 160°. Similarly, if thirty minutes' time were allowed, the temperature of initial action would be taken as below 160°, whilst with longer periods still yet lower temperatures would be deduced.

It is evident also from the preceding observations, that apparently trifling circumstances may so affect the physical condition of the metallic oxide examined, that no action at all may be noticed in a given

time sufficient under other conditions to bring about a considerable amount of action: thus, simply heating the copper oxide and allowing it to cool before use, largely extends the duration of the period during which no perceptible amount of action takes place. From these circumstances it appears that the results obtained in Reports I and II are, in some cases at any rate, open to the objection that the non-occurrence of action at any given temperature with any given metallic oxide, cannot be held to substantiate completely the rule deduced that the temperature of initial action is, *cæteris paribus*, the lower the greater (algebraically speaking) is the heat evolution occurring during the reaction; for the time of observation in each case was only some few minutes, rarely more than a quarter of an hour; whence, not only were numbers obtained at the temperatures of initial action probably considerably different from those that would have been obtained had the duration of the observations been longer, but also the negative results observed below certain temperatures might have been due to something abnormal about the physical state.

It is, therefore, highly desirable to check the conclusions arrived at from these short-time observations in another way: and this it seems probable can be done at any rate in certain instances by determining the character of the curves obtainable with different metallic oxides under the reducing influence of hydrogen and carbon oxide under uniform condition; if the reaction is influenced by the amount of heat that would be developed by its occurrence in such a way that the greater (algebraically) is this heat development the more readily does the action takes place (which is the essential idea embodied in the rule arrived at in Reports I and II, which for shortness may be referred to as the *dynamic rule*), it should result that the rate of reduction arrived at when the action is once started must be greater the greater the heat evolution: for example, under constant conditions as to temperature and general circumstances, the reduction of copper oxide by carbon oxide should go on more rapidly when once started than the reduction by hydrogen. It is, however, by no means inconceivable that the rate of action may be modified by certain circumstances and conditions which it is not possible to equalise in the two cases; for instance, the differences in diffusive power, viscosity, surface attraction to the metallic oxide, &c., &c., naturally existing between the two gases, may so influence the rate of action as to wholly interfere with the verification of the dynamic rule in this way; since these causes, if operative at all, are *à priori* more probably inclined to facilitate the reducing action of the hydrogen than of the carbon oxide, it would seem that, although the establishment of the circumstance that the rate of reduction by carbon oxide is greater than that by hydrogen, would considerably strengthen the evidence on behalf of the dynamic rule, the non-establishment of

this circumstance would not necessarily furnish an argument against the correctness of this rule.

It being, therefore, of interest to examine these points experimentally, the experiments above detailed were repeated with precisely the same conditions with the exception of the particular temperatures employed and of the use of carbon oxide instead of hydrogen as reducing agent. It has been already shown in Part II (p. 511), that when copper oxide from calcined nitrate is heated to 100° for some hours in an atmosphere of carbon oxide, CO_2 is formed in quantity, although the mere passage of the gas over the metallic oxide for a few minutes develops no CO_2 at temperatures below 125°; whence it appears probable that the phenomenon observed with hydrogen also occurs with carbon oxide, viz., that a certain length of time is requisite for the action to commence, this period of incubation, so to speak, varying in duration inversely with the temperature.

Considerable difficulty was experienced in producing anything like an equable current of carbon oxide: the gas, prepared from ferrocyanide of potassium and sulphuric acid, and purified as described in the previous reports, was stored in a gasometer over water, and when required for use was passed first through a bubbling apparatus to enable the bubbles to be counted, then through a red-hot tube containing charcoal, and finally through two potash-bulbs to absorb the carbon dioxide produced from the admixture of air necessarily present to some extent. The bubbling apparatus was filled with sulphuric acid to dry the gas, and prevent the formation of hydrogen in the red-hot tube from the reaction of the water vapour on the red-hot charcoal. The size of the bubbles was found to be seriously affected by the height of the water column forcing the gas out of the gasometer, being about 10 per cent. less when the water pressure was two feet than when it was three feet: as with hydrogen (§ 1) the quantity of gas delivered per 100 bubbles was considerably less when the gas passed slowly than when it passed more quickly: thus for instance, the following numbers were obtained with two different bubbling apparatus:—

Apparatus A.		*Apparatus B.*	
Time of passage of 100 bubbles in seconds.	c.c. of gas at 0° and 760 per 100 bubbles.	Time of passage of 100 bubbles in seconds.	c.c. of gas at 0° and 760 per 100 bubbles.
35	7·9	50	18·7
50	7·0	60	17·5
60	6·8	100	16·3
125	6·4		

Another source of difficulty arose from the circumstance that the gas employed, being collected and stored over water, was never abso-

lutely free from admixed air, so that after passing through the red hot tube containing charcoal, small quantities of nitrogen were mixed with it. The average composition of the gas (after passing through the red-hot tube and potash bulbs) was found to be 96 per cent. of carbon oxide and 4 of nitrogen; other gases were carefully sought for, especially hydrocarbons, but no evidence of their presence obtained, saving that in one or two instances the numbers obtained pointed to the presence of a little cyanogen, and in one or two others of a minute quantity of free hydrogen. Neither of these gases, if present, would have interfered with the results found even had they been present in much larger quantity than that suspected to be present (1 or 2 per cent.): for the reducing action of hydrogen at most of the temperatures employed is so small as to be practically, if not entirely, imperceptible in the time of exposure allowed; whilst direct experiments made with cyanogen (prepared by heating mercuric cyanide) showed that the same is true for that gas also: to this point and other allied ones we hope to return in a future paper. The actual gas currents employed were so regulated as to pass on an average 13·0 c.c. of carbon oxide containing nitrogen or 12·5 c.c. of pure CO per minute measured at 0° and 760 m.

Experiments were first made to see if the current of gas was heated up to the temperature of the air-bath by passing through one heated limb of the **U**-tube employed before reaching the bend where the copper oxide lay: these were carried out in precisely the same way as those described in § 1 with hydrogen for a similar purpose, and with the same result, viz., no cooling effect on a thermometer was produced by the carbon oxide stream, proving that it was completely heated up. Similar experiments were also made, as with hydrogen, to see if the heat developed during reduction sensibly affected the temperature of the partially reduced copper oxide, with the following results, the temperature being 184·5°, *i.e.*, the highest employed: during the period of reduction between 3 and 13 minutes' exposure, the average scale-reading difference of the two thermometers was 0·73°, the thermometer exposed to the CO stream being the lowest: between 13 and 24 minutes the average difference was 0·57°; and between 24 and 35 minutes it was 0·68°: the difference when no current at all passed, or when the current was passing, but no copper oxide was in the **U**-tube, was 0·80°; so that in the first, second, and third of these three periods, the temperatures of the issuing gases were raised, 0·07°, 0·23° and 0·12° respectively: the middle period corresponds to the period of most rapid reduction, the whole of the oxygen being removed in less than 45 minutes. Practically, therefore, the development of heat during reduction, although perceptibly greater than that observed with hydrogen, was too small to produce any material heating of the copper oxide.

Owing to our stock of the particular sample of copper oxide used for the previous experiments being not very great, we were unable to perform as many experiments at each temperature as would have been desirable for the exact determination of the mean curves, since the experimental errors through inequality in the gas current were probably greater than was the case with hydrogen; the following numbers, however, exhibit quite sufficient accordance to enable fair approximations to mean curves to be drawn; since these were obtained with the same volume of gas per minute (12·5 c.c. normal), whilst the reducing powers of equal volumes of the two gases are equal, the carbon oxide figures are directly comparable with those obtained with hydrogen; the same average weight of copper oxide, 1·15 gram, was used in every experiment.

At temperatures of 130° and upwards, the curves deduced from interrupted observations, and those from uninterrupted ones, coincided, showing that under these circumstances interrupting the reduction for a few minutes so as to cool and weigh did not interfere with the action subsequently: but below 130° it was found that the results of interrupted experiments were always below those obtained by uninterrupted observations. It is specially noticeable that the great irregularities in action noticed with hydrogen at temperatures between 130° and 160° did not manifest themselves with carbon oxide at corresponding temperatures (*i.e.*, 100° to 130°), the effect of interruption being allowed for; probably this arises from the lower temperatures not affecting the physical condition of the copper oxide during the earliest part of the exposure, so much as was the case in the hydrogen experiments at the somewhat higher temperatures.

The following numbers were obtained:—

At 184·5°.

Time in minutes.	Percentage loss of oxygen.									Averages.	
										Uninterrupted.	Interrupted.
1½	0·43	—	—	—	—	—	—	—	—	0·43	—
2½	—	1·65	—	—	—	—	—	—	—	1·65	—
5	2·87	3·61	2·91	—	—	—	—	—	—	2·91	3·24
10	—	7·08	5·77	5·11	4·61	—	—	—	—	4·86	6·42
15	10·50	—	8·90	—	8·45	8·68	—	—	—	8·68	9·28
20	—	—	12·10	10·48	—	—	12·50	—	—	12·50	11·29
25	15·63	—	—	—	14·89	14·01	—	13·04	—	13·04	14·84
30	18·10	—	—	—	—	—	17·42	16·35	18·89	18·89	17·29
35	19·62	—	—	—	—	—	—	18·26	—	—	18·94
40	—	—	—	—	—	—	19·44	—	—	—	19·44

At 160°.

Time in minutes.	Percentage loss of oxygen.									Averages.	
										Uninterrupted.	Interrupted.
2½	0·45	0·40	—	—	—	—	—	—	—	0·42	—
5	2·08	1·58	1·13	—	—	—	—	—	—	1·13	1·83
10	—	4·44	—	2·95	—	—	—	—	—	2·95	4·44
15	8·08	—	—	—	9·13	—	—	—	—	9·13	8·08
20	—	10·21	9·06	8·85	—	10·13	12·69	—	—	11·41	9·37
25	13·08	—	—	—	—	—	14·78	—	—	—	13·93
30	—	—	—	14·32	17·30	—	16·34	15·91	—	15·91	15·98
35	17·92	—	—	—	—	—	—	17·73	16·62	16·62	17·82
40	19·36	—	—	17·87	—	—	—	18·94	18·01	—	18·54
45	—	—	—	19·61	—	—	—	—	—	—	19·61

At 130°.

5	0·08	0	0	—	—	—	—	—	—	0·03	—
10	0·69	1·35	—	—	—	—	—	—	—	—	1·02
15	2·91	—	4·22	2·86	—	—	—	—	—	2·86	3·56
20	6·04	5·32	—	—	5·54	—	—	—	—	5·54	5·68
25	8·09	—	8·46	—	—	6·42	—	—	—	6·42	8·27
30	11·83	10·12	—	9·98	—	—	13·09	—	—	13·09	10·64
35	14·22	—	11·89	—	—	—	—	—	—	—	13·05
40	16·18	14·37	—	—	13·60	—	—	14·37	—	14·37	14·72
45	—	—	14·32	—	—	15·98	18·07	—	—	—	16·12
50	—	17·53	—	—	—	—	—	18·12	18·22	18·22	17·82
60	—	18·26	—	—	18·19	—	—	—	18·91	—	18·45
65	—	—	—	—	18·45	—	—	—	—	—	18·45
70	—	19·39	—	—	—	—	—	—	—	—	19·39

On plotting these values for three temperatures, 184·5°, 160°, and 130° respectively, as was done for the corresponding hydrogen values (§ 1), it is evident that the mean curves deducible from the interrupted and uninterrupted observations practically coincide: from these curves the following values are deduced: the curves themselves are shown in Fig. 2, being marked A, B, and C respectively (dotted lines):—

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 5 minutes.
5	2·90	2·90	2·90	0·580
10	6·35	3·45	0·55	0·690
15	9·85	3·50	0·05	0·700
20	12·90	3·05	−0·45	0·610
25	15·40	2·50	−0·55	0·500
30	17·55	2·15	−0·35	0·430
35	19·60	2·05	−0·10	0·410

At 160°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 5 minutes.
5	1·80	1·80	1·80	0·360
10	4·50	2·70	0·90	0·540
15	7·35	2·85	0·15	0·570
20	10·20	2·85	0	0·570
25	12·80	2·60	−0·25	0·520
30	14·70	1·90	−0·70	0·380
35	16·40	1·70	−0·20	0·340
40	18·02	1·62	−0·08	0·324
45	19·61	1·59	−0·03	0·318
		At 130°.		
5	0·03	0·03	0·03	0·006
10	1·13	1·10	1·07	0·220
15	3·45	2·32	1·22	0·464
20	5·85	2·40	0·08	0·480
25	8·25	2·40	0	0·480
30	10·55	2·30	−0·10	0·460
35	12·70	2·15	−0·15	0·430
40	14·60	1·90	−0·25	0·380
45	16·00	1·40	−0·50	0·280
50	17·05	1·05	−0·35	0·210
55	17·80	0·75	−0·30	0·150
60	18·40	0·60	−0·15	0·120
65	18·92	0·52	−0·08	0·104
70	19·39	0·47	−0·05	0·094

The rate of supply of carbon oxide in these experiments being the same as that of hydrogen in the previous ones (12·5 c.c. at 0° and 760 m., capable of removing 0·7791 per cent. of oxygen from 1·15 gram of copper oxide per minute), the limit to which the curves gradually tend as the temperature rises is the same as that existing with the hydrogen curves, viz., the straight slanting line to the left in Fig. 2 (marked "limit").

Below 130° the results of interrupted experiments no longer coincided with those of uninterrupted observations; thus the following values were obtained at 118° and 100°, clearly showing that the greater the number of interruptions, the less is the total amount of reduction brought about in a given time.

At 118°.

Time in minutes.	Percentage loss of oxygen.						Uninterrupted observations only.
5	0	—	—	—	—	—	0
10	0·13	—	—	—	—	—	0·13
15	—	1·39	—	—	—	—	1·39
20	1·87	—	—	—	—	—	—
30	3·91	4·95	6·19	—	—	—	6·19
50	7·98	10·46	—	13·13	—	—	13·13
70	11·46	14·12	15·14	15·67	15·73	—	15·73
90	13·23	15·91	18·13	—	—	18·78	18·78
105	—	16·60	—	—	—	—	—
120	14·81	17·35	19·35	—	—	—	—
135	—	18·00	—	—	—	—	—
165	—	18·60	—	—	—	—	—
195	—	18·96	—	—	—	—	—

At 100°.

Time in minutes.	Percentage loss of oxygen.										Uninterrupted observations only.
30	0	0	—	—	—	—	—	—	—	—	0
45	—	—	0·17	—	—	—	—	—	—	—	0·17
60	0	0	—	0	0·18	—	—	—	—	—	0·09
75	—	—	0·48	—	—	1·26	—	—	—	—	1·26
90	0	0·07	—	—	—	—	1·30	—	—	—	1·30
120	0·13	—	—	—	—	—	—	7·72	—	—	7·72
150	0·35	—	—	—	—	—	4·35	10·86	—	—	—
180	—	—	—	—	—	—	—	—	11·93	—	11·93
210	—	—	—	—	—	—	5·91	15·54	—	—	—
240	—	—	—	—	—	—	6·44	—	—	17·10	17·10

At 83—84°.

Time in minutes.	Percentage loss of oxygen.					Uninterrupted observations only.
60	0	—	—	—	—	0
120	—	0·69	—	—	—	0·69
180	—	—	0·86	—	—	0·86
240	—	—	—	0·69	—	0·69
360	—	—	—	—	2·44	2·44

The curves marked D, E, and F (Fig. 2, dotted lines), represent the

mean curves deduced from the uninterrupted observations only. The following values are deduced from these mean curves :—

At 118°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 10 minutes.
10	0·15	0·15	0·15	0·015
20	2·60	2·45	2·30	0·245
30	6·20	3·60	1·15	0·360
40	10·00	3·80	0·20	0·380
50	12·50	2·50	−1·30	0·250
60	14·50	2·00	−0·50	0·200
70	16·10	1·60	−0·40	0·160
80	17·50	1·40	−0·20	0·140
90	18·80	1·30	−0·10	0·130

At 100°.

Time in minutes.	Percentage loss.	Difference.	2nd difference.	Percentage loss per minute in each consecutive 20 minutes.
20	0	0	0	0
40	0·03	0·03	0·03	0·0015
60	0·10	0·07	0·04	0·0035
80	1·25	1·15	1·08	0·0575
100	3·50	2·25	1·10	0·1125
120	6·20	2·70	0·45	0·135
140	8·80	2·60	−0·10	0·130
160	10·90	2·10	−0·50	0·105
180	12·70	1·80	−0·30	0·090
200	14·30	1·60	−0·20	0·080
220	15·75	1·45	−0·15	0·0725
240	17·10	1·35	−0·10	0·0675

At 83—84°.

Time in minutes.	Percentage loss.	Difference.	Percentage loss per minute in each consecutive hour.
60	0	0	0
120	0·30	0·30	0·005
180	0·65	0·35	0·006
240	1·00	0·35	0·006
300	1·45	0·45	0·0075
360	2·40	0·95	0·016

On comparing together these six curves they are found to present almost exactly the same characteristics as the corresponding curves above described obtained with hydrogen. The existence of "chemical

induction" to an extent varying inversely with the temperature is evident; each curve rises gradually to a point of contrary flexure, when the rate of action is a maximum, the only noticeable difference between the hydrogen curves and those obtained with carbon oxide being that whilst with the former the point of contrary flexure lies close to the point representing a removal of half the oxygen present, with the latter it lies sensibly lower down, at a point corresponding to a removal of from two-fifths to three-sevenths of the oxygen present. This difference, doubtless, is due to the more easy permeability of the film of reduced copper or of cuprous oxide on the surface of the particles by hydrogen than by carbon oxide, owing to the greater diffusive power of the former. The rates of reduction (percentage loss of oxygen per minute) arrived at when the action is most rapid, corresponding to the points of contrary flexure, are:—

At 184·5°	0·70 per cent. of oxygen removed per minute	out of 19·74 per cent. originally present.
„ 160	0·57	„ „
„ 130	0·48	„ „
„ 118	0·38	„ „
„ 100	0·135	„ „
Possible maximum	0·779	„ „

When these curves are employed to construct a surface as described in § 1, the following numbers are obtained by taking sections of this surface in the manner there referred to.

Amount of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	Temperatures.					
	At 83—84°.	At 100°.	At 118°.	At 130°.	At 160°.	At 184·5°.
5	No action at all in 70 minutes.	0	0	0·03	1·80	2·90
10		0	0·15	1·13	4·50	6·35
15		0	1·20	3·45	7·35	9·85
20		0	2·60	5·85	10·20	12·90
25		0	4·10	8·25	12·80	15·40
30		0·01	6·20	10·55	14·70	17·55
35		0·02	8·10	12·70	16·40	19·60
40		0·03	10·00	14·60	18·02	—
45		0·04	11·40	16·00	19·61	—
50		0·06	12·50	17·05	—	—
55		0·08	13·55	17·80	—	—
60		0·10	14·50	18·40	—	—
65		0·30	15·35	18·92	—	—
70		0·60	16·10	19·39	—	—

Lengths of Time in Minutes required to produce given amounts of Deoxidation at different Temperatures.

Percentage of oxygen removed (19·74 p.c. originally present).	Times.					
	At 83—84°.	At 100°.	At 118°.	At 130°.	At 160°.	At 184·5°.
1	240	78	13	9	3	2
2	340	88	18	12	5	4
3	—	96	22	14	7	5
4	—	104	25	17	9	6
5	—	112	28	19	11	8
6	—	119	31	21	13	9
7	—	126	33	23	15	11
8	—	134	35	25	16	12
9	—	142	37	27	18	13
10	—	151	40	29	19	15
11	—	161	43	31	21	16
12	—	172	47	33	23	18
13	—	183	52	35	25	20
14	—	195	57	38	28	22
15	—	208	63	41	31	24
16	—	222	69	45	34	26
17	—	238	75	50	37	28
18	—	—	82	57	40	31
19	—	—	92	66	44	34

As a check upon the approximate accuracy of these values, the volumetric experiments described in § 1 were repeated, using carbon oxide instead of hydrogen. The following numbers indicate that, as with hydrogen, a tolerable proof of the correctness of the curve values is thus obtainable. The values of x given below are deduced from the curve numbers just quoted, in precisely the same way as that employed with hydrogen, *i.e.*, they are the numbers corresponding in the tables of mean curve values to the rates of reduction per minute for the percentage loss of oxygen represented by the mean between the loss at the beginning of the observation and that at the end. The following numbers were obtained :—

At 130°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of CO converted into CO_2.	
		Observed.	Calculated from formula 128·3 × x.
5·0	0·47	60·2	60·3
9·6	0·47	59·7	60·3
14·0	0·40	52·1	51·3
17·2	0·20	27·1	25·7
18·1	0·14	18·1	18·0

At 160°.

Mean percentage loss of oxygen during experiment.	Corresponding value of x from mean curve.	Percentage of CO converted into CO_2.	
		Observed.	Calculated from formula $128{\cdot}3 \times x$.
5·5	0·55	71·0	70·5
7·3	0·57	71·5	73·1
11·6	0·53	64·5	67·9
13·0	0·50	61·5	64·1
16·1	0·35	44·9	44·9
	At 184—5°.		
5·9	0·68	88·5	87·2
6·7	0·69	88·0	88·5
8·0	0·70	91·8	89·8
10·9	0·65	77·5	83·4
14·0	0·55	62·0	70·6

On comparing together the two surfaces thus described with carbon oxide and hydrogen, it is at once noticeable that *the former surface lies wholly outside the latter one.* This fact may be translated into the following proposition, which is evidently a large amplification of the rule deduced in Parts I and II from experiments, lasting a few minutes only (viz., that the reducing action of carbon oxide first becomes manifest at a lower temperature than that of hydrogen):—"When the reducing action of a given amount of carbon oxide, exerted in a given time on a given quantity of copper oxide, is compared with that exerted by the equivalent quantity of hydrogen (one fourteenth of its weight, or an equal bulk when measured under the same conditions) in the same time, on the same quantity of copper oxide, and under the same conditions throughout, the former is always greater than the latter; whilst the period of time required to produce a given amount of deoxidation by the carbon oxide, the temperature being constant throughout, is less than that required with the hydrogen; and the temperature requisite to produce a given amount of deoxidation in a given time is less with the carbon oxide than with the hydrogen." Further, if the rates of deoxidation attained when certain definite amounts of oxygen have been removed be compared in the two cases when the reduction is effected by carbon oxide and by hydrogen, the temperature being the same in each case, the rate in the former case is uniformly greater than that in the second. Thus at the temperature of 184·5°, the following figures are obtained:—

Percentage loss of oxygen at end of experiment.	Rate of deoxidation (percentage loss per minute) attained to at end of experiment.	
	With hydrogen.	With carbon oxide.
3·0	0·195	0·59
6·0	0·245	0·68
9·0	0·265	0·70
12·0	0·27	0·63
15·0	0·23	0·52
18·0	0·09	0·42

Similarly, at 160°, the following values are obtained :—

3·0	0·09	0·44
6·0	0·11	0·55
9·0	0·12	0·57
12·0	0·11	0·53
15·0	0·08	0·38
18·0	0·04	0·32

and so on for other temperatures, the results being deducible by interpolation from the tables given above.

It does not seem to follow necessarily in every case that when the "dynamic rule" is true (that in comparable cases action during a few minutes becomes first manifested at a lower temperature the greater the algebraic value of the heat evolution occurring during the action), these extensions of it will also be true; for it is easily conceivable that the rate at which the action goes on after being once started, is influenced by various circumstances besides the amount of heat generated in the action; thus physical differences in the reducing agents may exist which it is impossible to equalise in different cases (*e.g.*, difference in density, and consequently in rate of diffusion; differences in the surface attraction for the metallic oxide, condensibility therein or thereon, &c., and so on), and these differences may possibly in some cases influence the rate at which the action proceeds so largely as to overpower the influence of the heat evolution [that the differences in diffusive power, &c., between hydrogen and carbon oxide do affect the rate at which reduction goes on, has been already indicated by the fact that the points of contrary flexure in the carbon oxide curves lie lower down than those in the hydrogen curves.] Similarly, analogous physical differences in the gaseous products of reduction (*e.g.*, steam and carbon dioxide), may influence the rate at which the action proceeds. Again, in certain cases there may be a tendency more or less marked towards the setting up of chemical changes other than the simple deoxidation of form—

$$AB + C = A + BC,$$

where B is oxygen, A B a metallic oxide, and C a reducing agent; and these tendencies, even if not sufficiently strong to cause these other changes to take place to a measurable extent, may yet interfere with the occurrence of the simple deoxidation at as rapid a rate as it would have gone on at had these different tendencies not existed. Thus for example when oxides of iron are deoxidised by hydrogen, there is a more or less strongly marked tendency towards an inverse reaction of the nature of the following:—

$$(1.)\quad 3Fe + 4H_2O = Fe_3O_4 + 4H_2,$$

i.e., towards a reoxidation of the metal and the formation of free hydrogen from the steam produced. Similarly, when carbon oxide is the reducing agent, there is an analogous tendency to an inverse reaction of the form—

$$(2.)\quad 3Fe + 4CO_2 = Fe_3O_4 + 4CO,$$

and it does not necessarily follow that at any given temperature the influence of the first inverse tendency in reducing the rate of reduction by hydrogen is equal to the influence of the second inverse tendency in reducing the rate of reduction by carbon oxide.

Again, in the case of reduction of iron oxide by carbon oxide, there exists a more or less strongly marked tendency towards the setting up of a reaction of the form—

$$Fe_xO_y + CO = Fe_xO_{y+1} + C$$

(Lowthian Bell, "Chemical Phenomena of Iron Smelting," page 44, *et seq.*), *i.e.*, towards the occurrence of a chemical change, wholly different from the one of simple deoxidation, expressed by equation (2); and the existence of this tendency, even though it may not be sufficiently strong to cause the deposition of a weighable amount of carbon, is yet likely to diminish the rate at which the deoxidation of the iron oxide by carbon oxide would otherwise take place.

Yet again, with many metallic oxides there is more or less tendency for the oxide to combine with the carbon dioxide (perhaps whilst still nascent), so as to form a carbonate; and this tendency, whether sufficiently strong to cause the formation of recognisable quantities of carbonate or not, must necessarily influence the rate of the action of the carbon oxide on the metallic oxide.

From considerations such as these, therefore, it results that it is not always possible to predict *a priori* what will be the relationships of the curved surfaces indicating the relations between deoxidation, time, and temperature in the case of any two reducing agents and a given metallic oxide, or between any two metallic oxides and a given reducing agent. This much can be deduced from the experiments described in Reports I and II, that the points where the surface just begins to

rise perceptibly above the basal plane probably correspond, for equal times, to lower temperatures in the case of the substances which evolve most heat (or absorb least) during their reaction; and probably similarly correspond, for equal temperatures, to shorter times in these cases; but it cannot be predicted with certainty that this must be the case, and still less that the one surface will lie wholly outside the other, the two never cutting; this may be the case where disturbing influences are but small compared with the influence of the amount of heat generated during the reaction (copper oxide, with hydrogen and carbon oxide, seems to be an instance of this), but it may be otherwise when the disturbing influences are greater relatively; from experiments now in progress on the character of the curve surfaces obtained with ferric oxide and hydrogen and carbon oxide, it seems probable that these surfaces are to some extent instances of the latter kind. The discussion of these, and other analogous results, will be referred to in a future report.

§ 3. *Experiments on the Reduction of Copper Oxide by Carbon Oxide and Hydrogen at comparatively Low Temperatures in Sealed Tubes.*

The experiments above described indicate that the lower the temperature the greater is the length of time which must elapse before the amount of reduction taking place becomes measurable, this being the case both when hydrogen and when carbon oxide is the reducing agent. The form of apparatus used did not conveniently lend itself to carrying out experiments for a longer period than some six or seven hours, so that in order to obtain information as to the relative amounts of time required to produce a measurable amount of reduction by hydrogen and by carbon oxide when these lengths of time were considerable, an entirely different mode of experimenting was adopted, consisting in sealing up the copper oxide in glass tubes in an atmosphere of the reducing gas (the tubes being heated to the required temperatures before finally sealing, to avoid any material variation in pressure in the different experiments), and then keeping at the required temperature for a given time, cooling, opening the tubes, and examining the copper oxide to see if reduction had taken place (and in the carbon oxide experiments examining the gas in the tube to see if carbon dioxide had been formed).

It is evident that the results of experiments made in this way could not be directly compared with those obtained in the **U**-tube apparatus; for in the latter case a continuous current of reducing gas was perpetually passing over the copper oxide, and as shown above, the rate of reduction depends on the current speed (*cæteris paribus*); whilst the sealed tube experiments might be taken as a kind of limiting case of

the **U**-tube observations when the current speed was 0; so that of necessity it should result that reduction to a measurable extent should be brought about at a given temperature more quickly in the **U**-tube experiment than in the sealed tube observations. That this is so, the following results clearly prove; since, however, all the sealed tube experiments were conducted in the same way, the results obtained in this series of observations are strictly comparable among themselves. As will be seen on inspecting the results detailed below, the time required to produce a just measurable amount of action at a given temperature is considerably less in an atmosphere of carbon oxide than in one of hydrogen.

The sealed tubes employed were about 5 to 6 inches long, and held 10—15 c.c.: a piece of carefully cleaned and dried glass tubing having been drawn out to a capillary tube at one end, and this end blocked with a plug of glass-wool, about 0·5 gram of copper oxide was introduced, and the other end drawn out to a similar capillary. By means of india-rubber tubes the glass tube was then connected with the exit pipe of a current of purified hydrogen (or carbon oxide) so as to displace the air, the gas being admitted at the end not plugged; the plugged end was then sealed by the blowpipe, and the india-rubber tube connecting the other end to the gas supply tightly clamped. The tube was then quickly transferred to the vapour-bath, the clamp just opened to allow the expanded gas to escape, and the projecting capillary tube sealed by the blowpipe. The vapour-baths employed were usually flasks containing a liquid of tolerably constant boiling point, and furnished with an inverted condenser; for some of the lower temperature observations, however, a water or paraffin-bath furnished with a Page's regulator was used, the sealed tubes being sunk nearly to the bottom of the warm fluid by a weight attached by a wire, in such a fashion that the tube could not get overheated by contact with the bottom of the bath, nor partially cooled by floating above its surface.

In titrating the copper oxide after the experiment allowance was, of course, made for the small quantity of permanganate required by the copper oxide itself previously to any further reduction, owing to its possessing the average composition not of pure CuO, but of $Cu_{40}O_{39}$ (§ 1). Owing to this correction being requisite and other unavoidable experimental errors, it was found impossible to determine accurately a subtraction of oxygen of much less than 0·00025 gram; but this quantity, corresponding to about ·25 c.c. of the weak permanganate solution employed, and to about 0·05 per cent. of oxygen removed, could be recognised pretty readily; in most cases, however, the amount of reduction taking place, if measurable at all, greatly exceeded this limit. In the experiments with carbon oxide another test was

obtained by breaking off the ends of the sealed tube, and cautiously aspirating the gas through clear baryta-water to see if any carbon dioxide were formed. It very frequently happened that traces of turbidity were thus caused, even though no evidence could be obtained of any reduction on titration; but we are inclined to attribute this not so much to true reduction in an incipient stage as to the possible action of the oxygen of the trace of air present (as a film on the surface of the copper oxide and glass tube mechanically condensed thereon) on the carbon oxide, much as spongy platinum causes the combination of hydrogen and oxygen by condensing them within its pores. The capacity of the sealed tube being approximately known and the quantity of oxygen removed, the approximate percentage of reducing gas oxidised is readily calculated.

The following results were obtained:—

At 160° (*corrected*).

Carbon oxide.

Time in minutes.	Percentage of oxygen removed determined by titration.	Baryta test for carbon dioxide.
5	0	—
10	0	—
15	0·28	copious

In this last experiment about 25 per cent. of the CO present was converted into CO_2.

Hydrogen.

Time in minutes.	Percentage of oxygen removed determined by titration.
25	0
35	0
45	0
60	0
75	0
88	0·59
105	0·61
125	0·12

At 130°.

15	0	—
25	0	—
30	0	—
40	0·64	copious
60	0·98	copious

In these two last experiments about 60 and 85 per cent. of the CO present was converted into CO_2 respectively.

120	0
180	0
255	0·05
300	1·24

In this last experiment about 94 per cent. of the hydrogen was converted into H_2O.

At 108°.

Time in hours.	Percentage oxygen removed.	Baryta test.
1	0	—
2	0	—
2·5	0	—
3	0	—
3·5	0	—
4·5	0	—
6	0	—
6·5	0·61	copious
7·0	0·84	copious

Time in hours.	Percentage oxygen removed.
3	0
4	0
5	0
8	0
10	0
14	0·18
17	0·30
18	1·07

In this last experiment upwards of 90 per cent. of the hydrogen was oxidised to water.

At 100°.

0·5	0	—
0·75	0	—
1·0	0	—
1·5	0	—
2·0	0	—
3·0	0	—
6·0	0	—
7·0	0	—
8·0	0·50	copious
10·0	0·70	copious

18	0
24	0
27·25	0
30	0·11
39	0·81

In this last experiment about 80 per cent. of the hydrogen was oxidised to H_2O.

At 83—84°.

2·5	0	—
4·0	0	—
5·0	0	—
8·0	0	—
13·25	0·20	considerable
17·5	0·41	copious
21·0	0·76	copious

In these three last experiments, the amounts of CO converted into CO_2, were respectively about 15, 30, and 90 per cent. of the total quantity present.

42	0
51	0
69	0
112	0
143	0
167	0
190	0·12
216	0·07
256	0·07
292	0
335	$\begin{cases} a = 0{\cdot}64 \\ b = 0{\cdot}36 \end{cases}$

On comparing together these results, it is evident that in all cases they are fairly concordant, the only apparent exception being in the case of the experiments at 83—84° with the hydrogen tubes, when one experiment after 190 hours gave a notable amount of reduction, two after 216 and 256 hours respectively a lesser amount, but one after 292 hours no action at all. It is hence evident that the following

times may be taken as close approximations to the periods which elapsed in the different cases before reduction went on to an extent great enough to be measurable :—

Temperature.	Carbon Oxide.	Hydrogen.
At 160° ...	Between 10 and 15 m., say 12 m.	Between 75 and 88 m., say 80 m.
„ 130 ...	„ 30 and 40 m., „ 35 m.	A little less than 255 m., „ 230 m.
„ 108 ...	„ 6 and 6·5 h., „ 6·25 h.	Between 10 and 14 h., „ 12 h.
„ 100 ...	„ 7 and 8 h., „ 7·5 h.	„ 27·25 and 30 h., „ 28 h.
„ 83—84.	Somewhat less than 13·25 h., say 11 h.	„ 167 and 190 h., „ 180 h.

That is to say, the length of time required to elapse before a measurable amount of reduction takes place, *is uniformly greater the lower the temperature with the same reducing agent and metallic oxide; and is less with carbon oxide than with hydrogen for the same temperature and metallic oxide.*

These time-values also illustrate the great effect which variation in current speed of reducing gas produces. As already indicated the sealed tube values may be taken as being the times requisite for a current speed of 0. The following table gives the relation between these times and those observed with the normal current of 12·5 c.c. per minute (§§ 1 and 2) in the **U**-tube experiments.

Temperature.	Carbon Oxide.		Hydrogen.	
	Sealed tube.	**U**-tube.	Sealed tube.	**U**-tube.
160°	About 12 mins.	Less than 2·5 mins.	About 1·3 hrs.	About 0·5 hr.
130	„ 35 „	About 5 „	„ 3·9 „	„ 2 „
118	„ 6·25 hrs.	„ 8 „	„ 12 „	More than 7 „
100	„ 7·5 „	„ 40 „	„ 28 „	„ „ „
83—84 ...	„ 11 „	—	„ 180 „	—

It is noticeable than the difference seems to be more marked with carbon oxide than with hydrogen.

A check on the above observations made at 100° in hydrogen was obtained in another way. A piece of quill tubing some 30 inches in length was bent to a double right angle like a **U**, but with one limb much longer than the other; about a gram of copper oxide was introduced and shaken down to the middle part of the **U**, the limbs being vertical and pointing upwards. The air was then displaced by hydrogen, and the shorter limb sealed by the blowpipe, the india-

rubber tube connected with the other limb being clamped tight. As soon as the sealed-up end was cold, the oxide of copper was shaken to the sealed part, and the **U**-tube held so that the limbs pointed downwards; the sealed end was then passed through a hole in the cork of a flask containing boiling water and furnished with a condenser; the other end was then opened under mercury. After the first few seconds, when hydrogen rushed out at the open end owing to expansion, no perceptible alteration in the level of the mercury took place for 28 hours; but after 44 hours the mercury had risen some inches in the limb dipping under mercury, and continued steadily rising. The tube was marked at different points corresponding to the position of the mercury after various lengths of time, and when the experiment was finished, the tube was roughly calibrated by pouring in water from a burette, so as to determine the amount of diminution in bulk of the hydrogen owing to its conversion into steam and the condensation of this in the cooler part of the tube; the copper oxide was also titrated by permanganate after the end of the experiment. The following numbers were obtained, the diminution in bulk of hydrogen being calculated to weight of oxygen removed:—

After 28 hours, oxygen removed	= 0	
„ 44 „ „	= 0·63	per cent.
„ 47 „ „	= 0·82	„
„ 50 „ „	= 1·04	„
Oxygen removed after 50 hours (by titration) ..	= 1·03	„

Judging from the rate at which the diminution of the hydrogen progressed, the action must have been first commenced after between 30 and 35 hours, about 29 hours being the time found in the sealed tube experiments.

§ 4. *Experiments carried out in an Atmosphere containing an excess of Reducing Agent.*

Some experiments were also made with a view to determine the rate at which deoxidation of copper oxide goes on under such conditions that the vessel containing the copper oxide always contained more reducing gas than would suffice for complete reduction. To effect this a weighed quantity (close to 0·2 gram) of copper oxide was dropped into a bulb-tube or spherical flask holding some 300 c.c. immersed in a vapour-bath of the required temperature, and after a given time the bulb and contents were removed from the vapour-bath, cooled down, and the partially reduced copper oxide was dissolved up in a measured quantity of slightly acid ferric chloride solution, diluted with water and titrated by permanganate. In order to avoid entrance

of air during the introduction of the copper oxide, the reduction thereof, and the cooling down of the whole, a current of the reducing gas employed was admitted into the bulb by a small glass tube fused through the side of the bulb and dipping downwards inside almost to the bottom, in such a position that as the experiment proceeded the steam or carbon dioxide formed must have been mostly displaced by the entering gas as fast as formed. This glass tube was curled round the bulb externally so that the entering gas should be thoroughly heated to the temperature of the vapour-bath before entrance. Into the mouth of the flask was fitted a cork carrying a thermometer and a thistle-funnel, down which the copper oxide was poured (the current of reducing gas being momentarily stopped) at a noted time when the thermometer indicated that the flask and contained gas had reached the temperature of the vapour-bath.

It was found, however, that no good concordant results were obtainable; the rate at which the reduction proceeded in hydrogen appeared to be variable with the rate at which the entering reducing gas passed over the surface, and in particular the period of time which elapsed before any appreciable amount of action took place varied considerably even when all the conditions were apparently the same or nearly so.

The reduction commenced visibly by the formation of a red speck amongst the little mass of copper oxide at the lowest part of the bulb; this quickly spread, becoming rapidly larger and larger until practically the whole mass became a reddish metallic powder, the progress of the action reminding one of the slow deflagration of a quantity of touch-paper, the reducing action being apparently propagated from particle to particle throughout the mass. For this reason the action went on for some seconds or more after removal of the bulb from the vapour-bath, and nothing like an accurate time-correction could be made.

A different specimen of copper oxide was employed in these observations owing to the former batch being used up. This was prepared in the same way, but was not ignited over the blowpipe; the nitrate, partially decomposed by heating in an open basin to below a red heat, was heated to redness in a combustion-tube in a current of air for some two hours. The product was affected by hydrogen at 184·5° in almost exactly the same way as the specimen used for the previous experiments, with only this slight difference, that the period of time elapsing before action commenced to an appreciable extent was somewhat longer, so that the curve traced out on repeating the **U**-tube experiments lay a little to the right hand of the mean curve deduced above from the experiments with the first batch. Thus the following numbers represent the difference:—

Time in minutes.	Percentage of oxygen removed. New batch of copper oxide.	Old batch (from mean curve, *supra*).
20	0·79	0·93
40	3·78	4·71
80	12·33	14·93
110	18·03	18·65

This new batch of copper oxide was sensibly pure copper monoxide, CuO, as it was found to contain 20·05 per cent. of oxygen, and caused only a very small amount of reduction in dilute slightly acid ferric chloride solution on boiling therewith, the amount of oxygen deficiency from that corresponding to CuO, deduced on titration with permanganate being only 0·08 per cent.

With carbon oxide the results obtained were not so discrepant as with hydrogen. With the latter it often happened that in some experiments complete reduction was brought about in a time much less than that in which, in other experiments, no action at all took place, so that no curve-values could be deduced. With the former the following numbers were obtained at 130° and similar ones at other temperatures:—

Time in minutes.	Percentage of oxygen removed.
10	0
15	0
15	0
18	10·0
20	7·7
20	10·4
25	15·6
30	14·8
32	14·5
40	16·0
45	18·0
60	18·6

These numbers are sufficiently concordant to show that the curve line representing the reducing action in an atmosphere containing a surplus of carbon oxide over the amount required for complete reduction is of the same general character as that representing the action in the U-tubes in which the copper oxide was in contact during any given small period of time with only a small fraction of the quantity requisite for complete reduction: *i.e.*, for some time no action at all takes place; the action then commences and rapidly increases to a maximum rate, and then diminishes in rate until complete reduction is brought about.

In other words, chemical induction takes place whether the reducing agent or the metallic oxide be in excess.

Experiments are now in progress by one of us and Mr. A. E. Menke as to the rate at which oxidation of spongy metallic copper goes on when heated in a known current of air to various temperatures. It would seem from the results already arrived at that in this case there is no chemical induction at all. The action begins as soon as the temperature is attained by the tube containing the metal, and goes on at a rate which is a maximum at first and then gradually diminishes, doubtless owing to the covering over of the particles of metal with an increasing film of oxide.

LIII.—*On Chlor-stannic Acid.*

By J. W. Mallet, F.R.S.

A bottle containing a pretty strong aqueous solution of stannous ride, which had stood upon the laboratory shelves for a year or two, occasionally opened, and never very tightly closed, had for some time been growing turbid, though no great quantity of the white insoluble stannous oxychloride had been produced. I observed lately that a soft solid layer of nearly transparent jelly-like material had formed at the bottom to the depth of about a centimeter. This colloid substance, of yellowish colour, was obtained in a nearly pure state by carefully decanting off the liquid from above it, lightly rinsing it in the undisturbed condition, and then, after breaking it up, with a little water, and finally removing it from the bottle to a glass plate, upon which it was allowed to dry at atmospheric temperature.

The small amount of washing to which most of the material was subjected seemed to produce no change upon it, but long continued treatment with water, particularly if hot, produced whitish turbidity, and obviously altered the chemical composition.

The substance, which while moist reddened litmus-paper, shrank greatly in bulk on drying, cracked asunder, and assumed the appearance of little fragments of pale-yellow gum arabic. When heated in a glass tube it gave off hydrochloric acid with a very little vapour of water, and left behind a white residue of stannic oxide free from chlorine, just the same result being observed when free oxygen was excluded, the tube being first exhausted of air by the Sprengel pump.

The supply of material was but meagre; it sufficed, however, for obtaining the following quantitative results:

·7253 gram gave off ·1396 gram of HCl and ·0092 gram of H_2O, and left behind ·5804 gram of SnO_2.

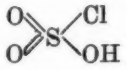
Assuming that the trifling quantity of water may be neglected, as resulting merely from imperfect drying, these figures correspond with the formula SnO_2HCl.

	Found.	Calculated.
SnO_2	·5804	·5804
HCl	·1396	·1412

and hence the constitutional formula may be inferred to be—

$$O=Sn<\begin{matrix}Cl\\OH\end{matrix}$$

or that of normal stannic acid with one hydroxyl replaced by chlorine, a true chlorine substitution-product from a metallic acid, analogous in structure to the chloro-hydrated sulphuric acid of Williamson (*Proc. Roy. Soc.*, **7**, 11)—



In order to test the possession of acid character, a solution of caustic soda was brought in contact with this substance, both in its fresh still moist condition and after drying. In both cases decomposition took place, sodium chloride being formed, and a white opaque powder produced, slowly dissolving in excess of the liquid. By using very weak solution of ammonia, however, no material change of appearance was produced; a little of the gummy mass dissolved, but most remained behind, and on drying this latter portion in the air after prolonged contact with the solution, heating the colloid material with a fixed alkali in a glass tube expelled gaseous ammonia.

·4409 gram heated with solid sodium hydrate gave off ·0395 gram of NH_3—the formula—

$$O=Sn<\begin{matrix}Cl\\O-NH_4\end{matrix}$$

requires ·0368 gram, tending to confirm the above view of the character of this substance.

The change experienced by the original stannous chloride may be supposed to have been—

$$SnCl_2 + H_2O + O = HCl + SnO\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$$

or else the usual formation of stannous oxychloride and stannic chloride from absorption of oxygen,

$$3SnCl_2 + O = Sn_2Cl_2O + SnCl_4$$

may have first occurred, followed by the reaction—

$$SnCl_4 + 2H_2O = 3HCl + SnO\begin{cases} Cl \\ OH \end{cases}$$

I have made several attempts in various ways to reproduce these results, but so far without success.

At the risk of a little confusion growing out of the name chlorostannates having been used for the double chlorides of tin and other metals, but as far as possible avoiding this by a slight change in the form of the prefix, the substance now described may properly be called chlor-stannic acid.

LIV.—*On the Action of Organo-Zinc Compounds on Quinones.* (Preliminary Note).

By Francis R. Japp, M.A., Ph.D., Assistant in the Chemical Research Laboratory, Science Schools, South Kensington.

Zinc-ethyl on Phenanthrene-quinone.

When finely-powdered phenanthrene-quinone is gradually added to zinc-ethyl, the latter being diluted with ether to such an extent as to be no longer spontaneously inflammable, a reaction takes place accompanied with evolution of gas. The orange colour of the quinone disappears; a whitish powder is formed, and sinks to the bottom of the liquid. The addition of quinone is continued so as to nearly exhaust the zinc-ethyl, care being taken, however, to leave the latter in excess.

In the first experiment performed in this way, the product of the reaction was decomposed by careful addition of water, which caused the evolution of torrents of gas. The zinc hydrate was removed by hydrochloric acid, and the substance which remained was dissolved in hot alcohol. The solution on cooling deposited large tabular crystals.

It was found, however, that these crystals could be prepared in a state of greater purity by decomposing the product of the zinc-ethyl reaction with alcohol, adding an excess of this solvent, boiling, and

filtering hot. The substance was thus obtained in transparent, almost colourless, rectangular plates, often nearly an inch long, sometimes free, sometimes grouped in rosettes. After once recrystallising from alcohol, they were sufficiently pure for analysis. Further recrystallising does not remove a faint yellowish tinge.

The crystals were pressed between folds of filter-paper, powdered, and dried by exposure for a short time to the air. Too long exposure is to be avoided, for reasons mentioned further on.

The following results were obtained on analysis :—

I. ·1821 gram gave ·5082 gram of carbonic anhydride and ·1151 gram water.

II. ·2024 gram gave ·5640 gram of carbonic anhydride and ·1253 gram water.

These numbers lead to the formula—

$C_{18}H_{20}O_3$.

	Calculated.		Found.	
			I.	II.
C_{18}.....	216	76·06	76·11	75·99
H_{20}	20	7·04	7·02	6·88
O_3.....	48	16·90	(16·87)	(17·13)
	284	100·00	100·00	100·00

The formula $C_{18}H_{20}O_3$ may be resolved into $C_{16}H_{14}O_2$, C_2H_6O. The compound $C_{16}H_{14}O_2$ has not yet been obtained in a state of purity, inasmuch as it has not been found possible to expel the last traces of alcohol without decomposing the substance, but the mon-acetyl derivative $C_{16}H_{13}O_2(C_2H_3O)$ has been prepared and analysed.

The air-dried substance $C_{16}H_{14}O_2,C_2H_6O$ employed in the above analysis fused at 77°, beginning to soften at 73°. It is readily soluble in all the ordinary solvents, with the exception of water, which dissolves only traces. When exposed to the air for some days in a finely divided state, it gradually assumes a deep orange tint, and is transformed into a gummy mass. In a vacuum these changes do not take place.

Acetyl-derivative.—The compound $C_{16}H_{14}O_2,C_2H_6O$ was boiled with acetic anhydride for some hours, after which alcohol was added to the liquid to decompose the excess of anhydride. On standing, the new substance crystallised from the solution in large, well-formed, colourless prisms. It was recrystallised twice from alcohol and twice from petroleum-ether (b. p. 70° to 100°). It fused at 103°.

Analysis yielded the following results :—

I. ·1601 gram gave ·4503 gram of carbonic anhydride and ·0798 gram of water.

II. ·1921 gram gave ·5416 gram of carbonic anhydride and ·0981 gram of water.

These numbers lead to the formula—

$$C_{18}H_{16}O_3 = C_{16}H_{13}O_2(C_2H_3O).$$

	Calculated.		Found.	
			I.	II.
C_{18}.....	216	77·14	76·70	76·89
H_{16}	16	5·71	5·54	5·67
O_3.....	48	17·15	(17·76)	(17·44)
	280	100·00	100·00	100·00

I refrain for the present from discussing the probable constitution of the compound $C_{16}H_{14}O_2$ and its relations to phenanthrene-quinone. I hope to be able to elucidate these points by an examination of its reactions. In addition to this, I purpose studying the action of organo-zinc compounds upon other quinones and upon allied substances, such as dibenzoyl. It is not inconceivable that these reactions may furnish a means of distinguishing between quinones proper and double ketones.

LV.—*On Indigo-purpurin and Indirubin.*

By Edward Schunck, Ph.D., F.R.S.

In a paper published several years ago, "On the Reduction of Isatin to Indigo-blue" (*Deut. Chem. Ges. Ber.*, **3**, 514), Baeyer and Emmerling mention a red colouring matter formed along with indigo-blue by the action of a mixture of acetyl chloride, phosphorus trichloride, and phosphorus on isatin in sealed tubes, to which they gave the name *indigo-purpurin*, because they supposed it to stand in the same relation to indigo-blue as purpurin does to alizarin. In a recently published memoir, "On the Action of Phosphorus Pentachloride on Isatin and on Allied Substances" (*ibid.*, **12**, 457), Baeyer describes another method of preparing this red colouring matter, of which he then gives the following description:—"It is easily soluble in glacial acetic acid, soluble in alcohol, ether, benzol, chloroform. When its solution in alcohol is mixed with water it separates in crystalline flocks. It crystallises from chloroform in ramified needles. The absorption spectrum of its solutions is characteristic, and entirely different from that of

indigo-blue. Indigo-purpurin is isomeric with indigo-blue, and is identical with the product obtained by Baeyer and Emmerling by the action of acetyl chloride, phosphorus trichloride, and phosphorus on isatin. It may be sublimed like indigo-blue, and also yields a vat, but it is much more permanent towards oxidising agents." Then follow the results of analyses, showing the substance to have the same composition as indigo-blue.

In a paper read before the Manchester Literary and Philosophical Society in 1856 (*Manchester Memoirs* [2], **14**, 181—237), I gave an account of a red colouring matter formed together with indigo-blue by the action of acids on indican, which I named indirubin. That indigo-purpurin and indirubin have the same general properties and are probably identical, the following extract from the paper referred to will show:—"Indirubin crystallises from its alcoholic solution in small needles, forming when dry a silky mass of a colour between purple and chocolate, which on being rubbed with a hard body shows a slight metallic lustre resembling that of bronze. When heated on platinum foil it emits red vapours, then melts, and burns with a yellow smoky flame, leaving some charcoal. When carefully heated between two watch-glasses it gives a yellowish-red vapour, which condenses on the upper glass in the form of long crystalline needles. These needles are plum- or garnet-coloured, and they possess a somewhat metallic lustre, which is however much inferior to that of indigo-blue. It dissolves completely in concentrated sulphuric acid, forming a purple solution, which when heated does not become black. The solution gives no precipitate with water, and after dilution imparts a fine purple colour to cotton, wool, and silk. When treated with nitric acid of ordinary strength, indirubin begins to dissolve even in the cold and to a greater extent on the application of heat, forming a purple solution, which on being further heated becomes red, and on boiling yellow. Very dilute nitric acid also decomposes and dissolves it on boiling, but its decomposition is effected with far more difficulty than that of indigo-blue by the same means. In like manner a boiling solution of bichromate of potash mixed with sulphuric acid, which easily decomposes indigo-blue, seems to have very little effect on it even when the boiling is continued for a considerable time. Indirubin is quite insoluble in alkaline liquids, but dissolves easily when a deoxidising agent, such as grape-sugar or a protosalt of iron or tin, is added at the same time. If it be treated, for instance, with a solution of protoxide of tin in caustic soda, it dissolves rapidly, forming a yellow solution, the surface of which on exposure to the air instantly becomes covered with a film of regenerated indirubin, the appearance being exactly like that of an indigo vat, except that the film floating on the surface is purple instead of blue. If a piece of calico be dipped into the solution and

then exposed to the air, it acquires a purple colour, which is not removed either by acids or soap." On being analysed, indirubin was found to have the same composition as indigo-blue.

In order to ascertain whether the two substances are distinct or not, I prepared some indigo-purpurin from isatin according to the directions given by Baeyer and Emmerling. The product I obtained was a colouring matter crystallising in needles, and having all the properties of indirubin from indican. There can be no doubt, therefore, it seems to me, regarding the identity of the two bodies. As it is desirable to avoid as much as possible increasing the number of synonyms in organic chemistry, it would be advisable I think to retain in this case the older name. The term indigo-purpurin is moreover inappropriate, the "purpurins" or trioxyanthraquinones being a well-defined class of bodies, of which purpurin from madder is the type.

In his last communication on the subject, Baeyer states that the product obtained by him contained indigo-blue, and the red colouring matter in various relative proportions, without mentioning the conditions under which one or the other is formed exclusively. I have myself, when describing the action of acids on indican, more than once referred to the circumstances in which indirubin is obtained in the place of indigo-blue. When a perfectly fresh aqueous solution of indican is mixed with any strong acid and heated, the substance splits up into indigo-blue and indiglucin. If, however, the solution be left to stand for a considerable time, or if it be boiled for a short time before the addition of acid, then a certain proportion of indirubin will be found accompanying the indigo-blue. The metamorphosis or molecular change which this indicates does not stop here. It goes on until at last the product of decomposition contains no indigo-blue whatever, and consists of indirubin only, generally mixed, however, with brown resinous bodies, the formation of which shows that a further change has taken place in the indican molecule.

LVI.—*The Composition of Cows' Milk in Health and Disease.*

By A. Wynter Blyth.

The object of this paper is to give the results of a research on the constituents of milk, which has occupied the author during the whole of the past winter. These results are shortly—

1. The separation of two alkaloïdal bodies as normal constituents of milk.

2. The separation of a third substance, probably a glucoside, derived from plants, &c., eaten by the cow.

3. A more complete, but still imperfect, quantitative estimation of the different constituents of milk.

4. The analyses of samples of milk derived from cattle in an unhealthy state, the object being to see if it were possible by the determination of every constituent to distinguish whether the source of a given sample of milk was healthy or the reverse.

1. *Isolation of the Milk Alkaloïds.*

It would be tedious to enumerate all the unsuccessful or partially successful methods attempted and abandoned for the separation of the alkaloids; it will suffice to say that on the removal of casein and albumin the alkaloïds may be isolated—

a. By precipitation with phospho-tungstic acid (Scheibler's reagent).

b. By precipitation with phospho-molybdic acid (Sonnenschein's reagent).

c. By precipitation with nitrate of mercury.

The first and second methods have been abandoned, on account of the unavoidable loss by decomposition when the precipitate is treated with hot baryta-water. The details of the actual process adopted are as follow:—

Separation by Nitrate of Mercury.—A litre of milk is divided into three equal parts, to one of which a litre of water is added. The casein is precipitated in a flocculent condition by the cautious addition of acetic acid, and to complete this precipitation carbonic anhydride is passed through the liquid for some time. On withdrawing the current of gas, most of the caseine will settle to the bottom of the vessel, leaving a yellow whey almost perfectly clear. The whey as far as possible is syphoned off, and the caseine collected on a fine sieve; with a little management the casein blocks up the meshes, and a perfectly clear filtrate is rapidly obtained. The filtrate is added to the liquid already syphoned off, and used to precipitate the second portion of the litre of milk, and similarly the last third of the litre is dealt with precisely in the same way and with the same fluid. The yellow whey is now boiled to get rid of the albumin, which is filtered off; the casein remaining on the sieve from the litre of milk is also boiled up with water and well pressed, the filtrate being added to the rest. In this way, and only in this way, can the casein and albumin be with any convenience or celerity separated from a large quantity of milk, the final liquid obtained not being more than twice the bulk of that originally operated on.

To the perfectly clear yellow whey a slight excess of the ordinary solution of nitrate of mercury used for urea estimation is added, and a dense flocculent precipitate falls.

This precipitate by nitrate of mercury has long been known, and was considered to denote the existence of a third albuminoïd, to which the name of lacto-protein was given.

Lacto-protein as a single simple definite substance has no existence, the precipitate by nitrate of mercury being a mixture of *galactin*, *lactochrome*, any trace of albumin which may still remain in solution, and similarly any trace of urea which the milk may have contained, all united with mercury.

On separation of the precipitate by subsidence and filtration, it is well washed and decomposed by hydrothion, the excess of which is got rid of in the usual way.

On filtering from the mercury sulphide the lead salt, a substance, to which I propose to give the name of *galactin*, is thrown down by the addition of acetate of lead; the precipitate at first coloured somewhat, may be obtained perfectly white and pure by successive decompositions and recompositions. It appears to have the following formula, $(PbO_{23})C_{54}H_{78}N_4O_{45}$.

	Found.	Calculated.
PbO	77·10	77·34
C	9·57	9·47
H	1·15	1·17
N	0·89	0·84
O	—	11·18

Galactin as obtained by decomposing the lead salt by hydrogen sulphide, presents the appearance of a white (or if slightly impure a fawn-coloured) brittle, neutral, tasteless, non-crystalline mass, soluble in water, and giving precipitates with the general alkaloïdal reagents of Sonnenschein and Scheibler. It is soluble in water, insoluble in strong alcohol.

After the liquid from which the galactin has been removed had been freed from the excess of lead by hydrogen sulphide, an alkaloïdal colouring matter, for which I propose the name of "*lactochrome*," may be separated by the addition of nitrate of mercury solution; the simplest formula of which appears to be, $HgOC_6H_{18}NO_6$:—

	Found.	Calculated.
HgO	51·97	51·92
C	17·42	17·06
H	4·32	4·32
N	4·0	3·46
O	—	23·34

A study of its decomposition-products may, however, show that its composition is more complicated than the above.

Lactochrome itself may be obtained by careful decomposition of the

mercury compound. As obtained by evaporating its solution in water or alcohol, it is in the form of bright red-orange resin-like masses, softening at 100° C., very soluble in hot alcohol, but partially separating as the liquid cools; it is freely soluble in water. Concentrated solutions give a simple spectrum, allowing most of the red and yellow rays to pass through. No bands were discovered (see Diagram).

SPECTRUM OF LACTOCHROME.

The amount of galactin in milk appears from 10 determinations to lie between ·15 to ·2 per cent.

The amount of lactochrome has not been estimated in any satisfactory manner, for it easily decomposes, and is difficult to purify. Attempts have been made to estimate the percentage by means of the mercury-compound, but since the results have varied from 0·1 to ·0001 per cent. in milks differing in no essential feature, it is obvious that the method indicated is untrustworthy; possibly a chromometric process would be successful.

2. *The Bitter Principle.*

When the milk has been freed from casein, albumin, and alkaloïds, and also from any reagents used to separate those substances, there yet remains a small quantity of a slightly bitter, neutral principle, which may be obtained from the alkalised liquid by precipitation with tannin, and subsequent treatment of the tannin compound in the usual way, with litharge, &c.

The details of a recent experiment undertaken to elucidate the nature of this substance are as follows:—

A commercial gallon of milk, measuring 3,800 c.c., was treated in successive proportions in the way indicated to free it from casein, albumin, and alkaloïds. Finally, the excess of mercury nitrate was thrown out by hydrogen sulphide, the liquid alkalised by ammonia, and precipitated by tannin, the precipitate was lastly washed, and then dried at 100° C. The dried powder was triturated with litharge in presence of alcohol, and finally the mixture was exhausted by boiling alcohol, filtered, and the filtrate evaporated to dryness. The substance was dissolved in water, and digested with animal charcoal, filtered, and evaporated to dryness. A dark sticky extract weighing 4 grams

was the result of these various and successive steps. From this about 20 mgrm. of minute white crystals were separated by absolute alcohol. 15 mgrams. of the crystals were burnt up with oxide of copper, and so far as such a small quantity can be trusted gave the empirical formula, CH_3O_5:—

	Found.	Calculated.
C	12·65	12·63
H	3·66	3·15
O	—	84·22

The larger portion was found to have the following properties:—A sticky dark brown-red extract, very hygroscopic (becoming quite fluid when exposed to the air in a short time), soluble in water in all proportions, insoluble in strong alcohol, reducing copper solution on boiling as well as chloride of gold at the ordinary temperature; it also rapidly reduced nitrate of silver solution when gently warmed. The taste was woody and feebly bitter. The reaction was neutral. Two strictly accordant analyses gave the empirical formula $C_3H_3O_4$.

	Found.	Calculated.
C	35·01	34·95
H	3·02	2·91
O	—	62·14

It is probable that these substances are decomposition-products of one and the same substance, and that they are derived from food eaten by the cow. However this may be, the fact remains that from more than 100 milks examined during the last winter, in no case has a tannin precipitate been wanting.

3. *Quantitative Estimation of the different Constituents of Milk.*

With regard to the total solid constituents of milk, the amount of milk-fat, the ash, and the percentage of what has been termed *solids* not fat, there is nothing new to offer, some thousands of analyses having definitely settled as much as a matter of the kind can be settled, the general and average proportions of those substances.

But it may be remarked, that the analyses of the analysts, as well as those of physiologists, only exceptionally show any determinations of the "albumin," and very erroneous statements have been made with reference to the percentage of albumin in milk.

It appears from my numerous analyses to vary as a rule within comparatively speaking small limits, and therefore should be more frequently estimated. The highest amount I have hitherto obtained was from milk derived from a healthy Devon cow, in which it reached 1·345 per cent.

The lowest in a cow suffering from phthisis 0·320 per cent.

In over 90 per cent. of the milk from healthy cows the percentage of albumin varied from 0·5 to a little under 1 per cent., the mean being 0·77 per cent.

Similarly the highest determination of casein was from a Guernsey cow, the highest being 4·8 per cent. The lowest from a cow suffering from phthisis, 2·9 per cent. The average amount of casein in healthy cows' milk appears to be very nearly 4·00 per cent.

The following table gives as complete a view of the relative proportions of the different bodies in cows' milk as at present is possible.

Average Composition of Healthy Cows' Milk.

			Parts per cent. by weight.
Milk fat ..	Olein	1·477....	3·50
	Stearin and Palmitin	1·750....	
	Butyrin	0·270....	
	Caproin, Caprylin and Rutin	0·003....	
Casein			3·98
Albumin			0·77
Milk-sugar			4·00
Galactin			0·17
Lactochrome			undetermined
Bitter principle (glucoside ?)			0·01*
Urea		traces, such as ·0001 per cent. nearly always present.	
Creatin		traces (Commaille).	
Ash	K_2O	0·1228	0·700
	Na_2O	0·0868	
	CaO	0·1608	
	Fe_2O_3	0·0005	
	P_2O_5	0·1922	
	Cl	0·1146	
	MgO	0·0243	
Water			86·87

Milk from Diseased Cows.—If the idea should be in part or wholly true, that consumption and similar maladies may be transmitted to man by the ingestion of milk from diseased cows, some method,

* Mean of four determinations only.

whether physical or chemical, of distinguishing such milks, becomes of the most vital importance. I have unfortunately had but few opportunities of working at this subject, but so far as the analyses to be quoted go, they rather appear to show that a cow even suffering from very acute disease may give milk, differing in no essential feature from normal milk, while, on the other hand, trivial and severe local affections of the udder, characterised by bloody or purulent discharges, are easily to be recognised, by the presence of such products in the milk.

Mammitis.—A Heifer, second day after Calving, suffering from Acute Mammitis.

Sp. gr. 1·0362.

	In 100 c.c.
Milk fat	2·800
Casein	4·025
Albumin	0·560
Milk-sugar	5·541
(Nitrate of mercury precipitate dried at 100°	1·68)*
Ash	0·920
NaCl in ash	0·920

The microscopical appearances did not differ in any essential feature from milk derived from cows having recently calved.

Parturient Apoplexy.—A Cow suffering from Parturient Apoplexy; Pulse Imperceptible; Temperature 99·4°. Third day after Calving.

Sp. gr. 1·037. Reaction feebly alkaline.

	In 100 c.c.
Milk fat	3·750
Casein	4·025
Albumin	1·145
(Weight of mercury precipitate	1·38)*
Ash	0·980
NaCl in ash	0·102

Urea was absent; there was much lactochrome. No abnormal elements detected by a microscopical examination.

* At the time of the analysis the compound nature of the mercury precipitate was not known.

The Milk of a Cow suffering from Pneumonia fourteen days after Calving. Pulse 82, *Temperature* 102·4°.

Sp. gr. 1·0297.

	In 100 c.c.
Milk-fat	2·965
Cholesterin	0·580
Casein	3·860
Milk-sugar	3·880
Albumin	0·430
Galactin	0·090
Urea	0·005
Ash	0·800
NaCl in ash	0·488

This is the only milk in which I have found cholesterin. The microscopical results were negative.

Engorgement of Rumen and Congested Liver. Pulse 68, *Temperature* 101°.

Sp. gr. 1·032.

	In 100 parts by weight.
Milk-fat	6·057
Casein	4·796
Albumin	1·067
Milk-sugar	4·497
Galactin	0·113
Ash	0·670
NaCl in ash	0·092

The milk appears simply concentrated.

Phthisis.—A Cow five years old with Extensive Tubercular Deposit in Right Lung. The Dam was also Scrofulous.

	Dec. 7, 1878.	Feb., 1879.
Sp. gr.	1·0297	1·0340
	In 100 c.c.	In 100 c.c.
Milk-fat	2·77	3·83
Casein	3·650	5·4
Albumin	0·867	0·365
Milk-sugar	2·824	3·34
Alkaloïds	?	? *
Ash	0·866	0·770
NaCl in ash	0·096	0·15

* The determinations of galactin were made on so small a quantity as not to be reliable, but this is certain that the galactin was beyond the average.

A careful microscopical examination could detect no abnormal elements.

Phthisis.—A Cow two years old in an advanced stage of Phthisis.

	Jan. 29.	Feb. 17.
Sp. gr.	1·0329	1·0335
	In 100 c.c.	In 100 c.c.
Milk-fat	2·599	3·280
Casein	3·000	3·980
Galactin	?	0·250
Milk-sugar	2·888	4·100
Ash	0·910	0·780
NaCl in ash	0·10	0·15

The entire amount the cow yielded in January was one gallon; the amount sent to me was a fractional part of the whole.

A Sample of Milk drawn from an Udder actually Infiltrated with Tubercular Deposit.

Sp. gr. 1·018.

	In 100 parts by weight.
Water	94·640
Casein	1·210
Albumin	2·387
Milk-sugar	0·470
Milk-fat	0·490
Alkaloïds	absent
Urea	0·039
Ash	0·764
NaCl in ash	0·430
Nitric acid in combination	0·018

The whole quantity of the fluid did not exceed 70 c.c. It was of a dirty amber colour, with the casein partially separating.

A microscopical examination showed very few fat globules, and the following abnormal elements:—

1. Clusters of oval or round granular cells, for the most part ·0005 inch in diameter, with a well marked oval nucleus.

2. Granular masses irregular in shape, varying in size from about 0·0006 inch to 10 or 12 times that size.

3. Granular rounded bodies, stained brilliantly by magenta or carmine.

This then is phthisical milk in its most intense form, and one never likely to be found in commerce, but admixture of such a fluid with genuine milk is possible.

It is essentially an albuminous serum, containing urea, small quantities of nitrates, common salt, and just sufficient casein and milk-sugar to show its origin from a much diseased milk-gland. The absence of alkaloïds is noteworthy.

Local affection of the Udder.—Milk from a Heifer two days after calving, suffering from retention of Fœtal Membrane, a portion of the Udder much inflamed.

The milk was pink in colour, and contained about a twentieth of its bulk of blood; it was perfectly fresh when examined, but rapidly putrefied. The blood was separated by subsidence as much as possible. The reaction was feebly acid:—

Sp. gr. 1·0313.

	In 100 c.c.
Milk-fat	4·40
Casein and milk-sugar	9·81
Albumin	0·62
Galactin	0·269
Ash	1·16

I have to express my thanks to Mr. George Gray, M.R.C.V.S., of Bakewell, Derbyshire, and to Mr. Penhale, M.R.C.V.S., Barnstaple, for the trouble they have taken in forwarding from time to time samples of milk.

LVII.—*Notes on the effect of Alcohol on Saliva, and on the Chemistry of Digestion.*

By William H. Watson, F.C.S.

Numerous experiments have been made as to the action of the different digestive fluids, and their active principles in the digestion of nutritive substances under various circumstances, but I have not been able to find that any results have been published showing the influence of alcohol upon the processes involved.

Casting to one side any opinions as to the actual influence of alcohol upon the *organs* which secrete the digestive fluids—this appears to be not directly under the domain of chemistry—the question asked, and which has suggested the experiments about to be described was, has alcohol any influence upon the rapidity with which the ferments act on the insoluble constituents of food? As yet, I have confined my

attention to the action of ptyalin, as being the most likely to be affected, and have left the peptic and pancreatic fluids for future investigations.

Certain points, however, suggest themselves, which render it improbable that these secretions will be much if at all affected by alcohol in the alimentary canal. With regard to the pancreatic juice, it is not likely that any active quantity of alcohol will reach the duodenum, where this fluid acts. We know that alcohol, whether possessing any value as a respiratory agent or not, is rapidly absorbed from the stomach, and appears almost immediately in the breath, apparently unchanged. The pepsin of gastric juice being combined with hydrochloric acid, and, certainly, in the instance of human beings accompanied by that acid in the free state, it is probable that the action of the gastric juice may not be much, if at all, affected by the presence of alcohol.*

The saliva and the pancreatic juice have alkaline reactions, and, from facts about to be stated, I think it very probable that the ptyalin of saliva exists combined, or partly so, with alkaline salts. Munk (*Chem. Centr.*, 1876, 622) shows that within certain limits both alkalis and acids increase the action of saliva, and as to acids I have made experiments which confirm this assertion. One drop, however, of hydrochloric acid, sp. gr. 1·60, added to 200 grains of saliva entirely stops the action.

The only mention I find bearing upon the action of alcohol on saliva is by Lehmann (*Physiol. Chem.*, **2**, 35), where he says: "We can hardly condemn an inquiry into the hypothetical diastase of saliva as absurd: for the saliva does not lose its property either by the action of heat or of alcohol, and pepsin similarly retains its power even after having been combined with salts of lead. This, however, is certain, that the pytalin obtained by Berzelius, Gmelin, and Wright was found in all cases to be deficient in the power of converting starch into sugar."

Cohnheimn first showed that pytalin may be precipitated from its aqueous solution by alcohol, but when redissolved by water it possesses its ferment action as before. This would suggest that *owing to the tendency of alcohol to precipitate the ptyalin from saliva*, it would retard the digestive action of that fluid; and the fact that when redissolved in water, pytalin exerts its previous action, suggests that the alcohol does not act upon it chemically by causing any decomposition or change of property. I find that pytalin is more rapidly or effectually precipitated from simple aqueous solutions than from saliva. The precipitation, or rather separation, is aided in both cases by heating to 100° F. Equal parts of saliva and alcohol, sp. gr. 0·830, were mixed,

* I find that pepsin is not thrown out of solution by alcohol, even from neutral solutions of it in hydrochloric acid.

and, after being kept for some hours at 100°, were allowed to stand for two days, and filtered. From the clear filtrate much of the alcohol was evaporated at 100°, and, afterwards a quantity of starch was added. After being kept at this temperature for two hours, the mixture was filtered, and the filtrate found to have a slight reducing action on cupric test, showing that the whole of the ptyalin had not been rendered insoluble. I can think of no clear reason why alcohol should be slower in precipitating the pytalin from saliva than from simple solutions of it in water, excepting that in the former case the ptyalin may be combined, the whole or part of it, with alkaline salts. It is suggestive. Wheat-starch in very fine powder was used in each of the following experiments. The mixed saliva being liable to vary as secreted at different periods of the day, I obtained sufficient upon each occasion to enable me to make two experiments—one as to the action of saliva alone upon starch; the other as to the rapidity of the action when saliva along with alcohol was used—the alcohol being added to the saliva just before the starch, and shaken. 200 grains by weight of saliva were used, and to this 10 grains of starch were added. In addition to this, in some of the experiments 25 grain-measures of alcohol, sp. gr. 0·830, were added (equal to about 18 grains of absolute alcohol), and in the rest, in order to make a just comparison, 25 grains of water were added. The mixtures were left in each instance for one hour at 100° F, after which they were diluted with water, and filtered as rapidly as possible. In portions of these filtrates the amount of extractive matter was determined, and in other portions the reducing action on cupric test.* This reducing action was calculated as due to glucose, though some of it would probably be due to other reducing agents.

1. *Extractive Matter.*

In order to arrive at the precise amount of extractive matter due to the action of the fluid under examination, it is necessary to deduct from the figures given below the amount of starch soluble in water under similar circumstances, and the amount of solids in the saliva used. I found 200 grains of water after acting upon the starch under similar circumstances to give 0·2 extractive matter. For the solids of saliva the following determinations were made per cent. :—

	Total solids.	Ash.	Loss on ignition.
Sample I	0·672	0·254	0·418
,, II	0·902	0·284	0·618
,, III	0·692	0·263	0·429

* An ammoniated cupric test was used giving reduction without precipitation, similar to that suggested by Dr. Pavy (*Chem. News*, Feb. 21st, 1879). I found it much more easily used than the cupric test as previously prepared with potash.

University of Michigan

Sample II contained a considerable quantity of mucus, hence the increase of total solids and organic matter. The total solids may be taken as 0·7 per cent. (average), and 1·4 therefore deducted from the following numbers, along with 0·2 for extractive matter due to water.

(*a.*) Extractive matter obtained by the action of saliva alone.

I	3·833	grains
II	3·700	„
III	3·500	„
Average.....	3·677	„

(*b.*) Extractive matter obtained by the action of saliva with alcohol.

I	2·800	grains
II	2·866	„
III	2·600	„
Average.....	2·755	„

(*c.*) Difference in the amounts of extractive matter obtained by the action of saliva alone, and by saliva with alcohol.

I	1·033	grain
II	0·734	„
III	0·900	„
Average.....	0·922	„

Thus, there was about one quarter less extractive matter produced when alcohol was used than when saliva was used alone.

2. *Glucose.*

(*a.*) The reducing action of the solution obtained by the action of saliva upon starch, calculated as glucose:—

I	1·200	grain	= 1·08	starch	dissolved
II	1·125	„	= 1·01 +	„	„
III	1·155	„	= 1·04 −	„	„
Average.....	1·160		= 1·04 +	„	„

(*b.*) The reducing action of the solution obtained by the action of saliva with alcohol upon starch, calculated as glucose:—

I	0·857	grain	= 0·77	starch	dissolved
II	0·803	„	= 0·72	„	„
III	0·780	„	= 0·70	„	„
Average.....	0·813	„	= 0·73	„	„

(*c.*) Difference.

I	0·343	grain	= 0·31	starch	dissolved
II	0·322	„	= 0·29	„	„
III	0·375	„	= 0·34	„	„
Average.....	0·347	„	= 0·313	„	„

It is now clearly seen that alcohol retards the digestion of starch by saliva, and this is probably owing to some of the pytalin being thrown out of solution and thus rendered inactive by the alcohol.

I thought it desirable, however, to determine whether the effect of alcohol was apparent when the saliva was mixed with a slightly acid fluid such as gastric juice, and for this purpose the saliva was acidulated by the addition of one drop of HCl, sp. gr. 1·16, to 400 grains. After being submitted to conditions as in the experiments already described, the following determinations were made :—

	Plain saliva.	Acidulated saliva.	Acidulated saliva with alcohol.	Difference between acidulated saliva and plain saliva.	Difference between acidulated saliva with and without alcohol.
Extractive matter	3·760	4·933	4·000	1·173	0·933
Glucose	1·234	1·708	1·331	0·474	0·377

The conclusions from these are (1) by the addition of the small amount of acid the action of the saliva is decidedly increased, and (2) the retarding influence of the alcohol is not lessened by the presence of the acid. Hence it follows that the saliva will be more active upon farinaceous bodies when mixed with the acid fluid of the stomach than it would otherwise be. Admitting, again, as the above experiments direct, that alcohol retards the digestion of farinaceous bodies by the saliva, we must see that by these bodies remaining undigested the gastric juice will be less able to act upon the albuminous substances: however, it is supposed on the other hand that alcohol excites the gastric glands to secrete more fluid, and, if so, then the latter surmise may be true only in theory and not apparently in effect.

Foster (*Watts' Dict. Chem.*, vol. v., p. 176) says "the addition of an acid" to saliva "first delays, then arrests, and finally destroys its action." I think some qualification is needed here.

Lehmann (*Phy. Chem.*, **2**, 34) concludes that "acids can no more impede the digestive power of saliva than alkalis can promote

it." He does not say anything about the effect of acid in very small quantities being to increase it, but he evidently considers—and in this he is in opposition to the later researches of Munk already quoted—that alkalis do not promote the action.

LVIII.—*A Contribution to the Theory of Fractional Distillation.*

By T. E. Thorpe, Ph.D., F.R.S.

Wanklyn, some years ago, drew attention to the fact that in the distillation of a mixture of liquids the proportion in which the constituents pass over depends not merely on their relative quantity in the mixture undergoing distillation, and on their respective vapour-tensions at the temperature of ebullition, but also upon their mutual adhesion and on the densities of their vapours. Wanklyn found that when two liquids of different boiling points were mixed together in equal quantities by weight, and subjected to distillation, the quantity of each constituent in the distillate was proportional to the product of its vapour-density and vapour-tension at the temperature of ebullition of the fraction. Hence under certain circumstances it may happen that the less volatile of the two substances will pass over most rapidly, that is, be found in largest quantity in the first fractions of the distillate. A mixture of 18 parts of methyl alcohol, boiling at 65·2° (v. d. 15·97) with 17 parts of ethyl iodide, boiling at 72° (v. d. 77·8) was distilled: the first third of the distillate contained 6 parts of methyl alcohol and 8·7 parts of ethyl iodide. If the vapour-tensions and vapour-densities of the two liquids are inversely proportional, the mixture will distil unchanged.

Similar observations have been made by others. Carey Lea found on heating a mixture of the hydrochlorates of ethylamine, diethylamine, and triethylamine with caustic alkali, that the whole of the triethylamine, the least volatile of the three bodies, was contained in the first portions of the distillate, provided that its proportion was not excessive.

Berthelot observed that a mixture of 90·9 parts of carbon disulphide boiling at 46·6° (v. d. 38) and 9·1 parts of ethyl alcohol boiling at 78·4 °(v. d. 23), behaved on distillation like a homogeneous liquid. The ratios obtained by multiplying the vapour-tensions and densities are 88·5 and 11·5. The difference is due to the mutual action of the two bodies on the total tension. It is well known that the tension of

a mixture of vapours is never equal to the sum of the tensions of the individual vapours. Berthelot found that if the original mixture contained less than 9·1 per cent. of alcohol, perfectly pure carbon disulphide would eventually be found in the distilling flask; if, on the other hand, the amount of alcohol exceeded this proportion, pure alcohol would ultimately remain.

I have recently noticed an instance of the same phenomenon sufficiently remarkable to merit investigation. A mixture of equal volumes of carbon tetrachloride (b. p. 76·6, cor., v. d. 76·7), and methyl alcohol (b. p. 65·2: v. d. 15·97) was distilled; 46·5 *per cent. of the whole boiled constantly between* 55·6° *and* 55·9°; *i.e., nearly* 10° *lower than the boiling point of the most volatile constituent.*

The composition of the mixture was ascertained by determining its vapour-density. Two independent estimations were made, with the following results:—

	I.	II.
Weight of liquid	147·7 mgrm.	147·7 mgrm.
Volume of vapour corrected for error of meniscus, expansion of glass, &c.	100·92 c.c.	100·80 c.c.
Temperature	99·60°	99·70°
Pressure	405·2 mm.	406·1 m.m.

	I.	II.	Mean.
Vapour-density	41·84	41·80	41·82

If x be the weight of methyl alcohol in 100 parts of the mixture, S_1, the vapour-density of methyl alcohol (H = 1); S_2, that of carbon tetrachloride, and S_3, that of the mixture; then

$$x = \frac{100(S_2 - S_3)S}{(S_2 - S_1)S_3},$$

and $100 - x$ gives the amount of carbon tetrachloride. The mean result gives—

Carbon tetrachloride	78·1
Methyl alcohol	21·9
	100·0

that is to say, a mixture of 1 part of methyl alcohol and 3·6 parts of carbon tetrachloride boils like a homogeneous liquid at about 10° lower than the boiling point of the methyl alcohol, the more volatile of the two liquids.

Further calculation shows that this proportion is almost identical with that obtained by multiplying the vapour-tensions of the two liquids at the temperature of the boiling point of the fractions (55·7°) by their respective vapour-densities.

According to Biot the relation of the vapour-tension of a liquid to its temperature may be conveniently represented by a formula of the form—

$$\text{Log F} = a + b\alpha^t + c\beta^t + \ldots\ldots$$

in which F is the tension in millimetres of mercury, and t is the temperature of the vapour (T), expressed in air-thermometer centigrade degrees $\pm$ a certain number.

Neglecting the last term, Regnault found for carbon tetrachloride—

$$\text{Log F} = 4{\cdot}193542 - 3{\cdot}9281281\ (\log \bar{1}{\cdot}9970602)^t$$
$$t = \text{T} + 20$$

and for methyl alcohol—

$$\text{Log F} = 5{\cdot}3214897 - 4{\cdot}3206220\ (\log \bar{1}{\cdot}9969288)^t$$
$$t = \text{T} + 14$$

Adopting Regnault's values for the conversion of the mercurial into air-thermometer degrees, t in the first equation may be taken as 76, and in the second as 70: hence the vapour-tensions of each constituent at the boiling point of the fraction will be—

Carbon tetrachloride	372·4 mm.
Methyl alcohol	487·4 „

and

v. t. × v. d.		v. t. × v. d.		Methyl alcohol.		Carbon tetrachloride.
478·4 × 15·97	:	372·4 × 76·69	::	1	:	3·67

Mr. Colman C. Starling, student in the laboratory of the Yorkshire College, continued the distillation of the liquid remaining in the flask, and estimated the proportion of the methyl alcohol and carbon tetrachloride in the several fractions by determinations of vapour-density. The results are as follow:—

Weight of mixed liquid taken, 100 grams. Its composition was:—

Carbon tetrachloride	66·6
Methyl alcohol	33·4
	100·0

Fraction.	Bar. mm.	Boiling point.	Weight of fraction. Grams.	Obs. v. d.	Percentage composition.	
					CCl_4.	CH_4O.
I.....	749·5	55·5—55·8°	46·49	41·82	78·05	21·95
II	„	55·8—56·2	10·21	40·55	76·56	23·44
III	„	56·2—56·5	6·94	39·62	75·39	24·61
IV.....	„	56·5—57·1	6·28	38·48	73·87	26·13
V.....	„	57·1—57·8	5·08	36·24	70·64	29·36
VI.....	760·7	57·8—58·8	1·64	34·62	68·04	31·96
VII.....	„	58·8—59·5	2·84	32·75	64·70	35·30
VIII.....	„	59·5—60·3	2·37	30·59	60·34	39·66
IX.....	„	60·3—61·1	1·86	28·44	55·37	44·63
X	„	61·1—61·8	1·48	26·47	50·09	49·91
XI.....	„	61·8—62·8	1·89	24·35	43·47	56·53
XII.....	„	62·8—63·8	1·99	21·42	32·13	67·87
XIII.....	„	63·8—64·8	2·53	18·45	16·97	83·03
XIV	„	64·8—65·5	2·75	16·55	4·41	95·59
Residue	„	65·6	4·80	15·94	0·00	100·00

These numbers show most clearly that the liquid of highest boiling point, viz., the carbon tetrachloride, passes over in largest quantity in the first fractions of the distillate, and that as the temperature rises the proportion of methyl alcohol gradually increases, until eventually the pure alcohol passes over.

A striking lecture-experiment illustrating the effect of the admixture of the two liquids is to fill three barometer tubes with mercury, and to pass up into the first a few drops of methyl alcohol, into the second a few drops of carbon tetrachloride, and into the third a small quantity of a mixture of methyl alcohol and carbon tetrachloride in the proportion of 3 c.c. of the former to 5 c.c. of the latter. In the first tube the mercury will be depressed about 80 mm.; in the second 70 mm.; whereas in the third, it will sink through 130 mm. This remarkable alteration in the tension is probably connected with certain physical peculiarities of the mixture, which will form the subject of a subsequent communication.

LIX.—*Theory of Fractional Distillation.*

By Frederick D. Brown, B.Sc.

Although the distillation of mixtures of volatile substances is one of the most ordinary chemical processes, the laws by which it is governed have remained without satisfactory explanation. The first step towards a solution of the question must, in this as in every other problem of natural science, be the accumulation of experimental results.

A perusal of the literature bearing directly or indirectly upon fractional distillation shows, however, a predominance of theoretical speculation and of technical rules, the former, built upon a very slender basis of experiment, the latter derived from, and designed for, the practical work of the distillery.

Before entering into a description of the experiments which I have made with a view to throw some light upon the matter, it will be well to consider carefully in what the process of distillation consists, in order that we may see, as clearly as possible, the object to be attained. Suppose then that we distil a mixture made up of certain weights, W_1, W_2, W_3, ... of various substances, A_1, A_2, A_3 . . . ; when the liquid begins to boil it will during a first infinitely small period of time emit a quantity of vapour, which may be represented by $V_1 + V_2 + V_3$ . . . . . ; the proportions of the different substances contained in this vapour will be dependent on the nature of A_1, A_2, A_3 . . . , on their relative proportions in the boiling liquid, and on the pressure at which ebullition takes place. We may assume that during the distillation neither the nature of the substances nor the pressure is subject to variation.

At the end of the first period, there will remain in the still $W_1 - V_1$ of A_1, $W_2 - V_2$ of A_2, &c.; if, therefore, the proportions of A_1, A_2, A_3, ... in the vapour are the same as in the boiling liquid, *i.e.*, if $\frac{W_1}{V_1} = \frac{W_2}{V_2} = \frac{W_3}{V_3} = . \ . \ . \ .$, the liquid remaining in the still will have the same composition at the end of the first period as at the beginning, the vapour given off during the second period will therefore contain A_1, A_2, A_3 . . . in the same ratios as in the first period, and so on throughout the distillation; the mixture will, in fact, distil like a single substance, and no separation of its constituent parts will take place. If, on the other hand, $\frac{W_1}{V_1}$, $\frac{W_2}{V_2}$, $\frac{W_3}{V_3}$, . . . be not all equal, the mixture will have altered in composition at the end of the first period, and the vapour emitted during the second period will contain A_1, A_2, A_3 . . . in new proportions determined by the new composition of the liquid. Since the same argument will apply to the other periods of the distillation, the composition of the liquid in the still and of the distillate at any period of the distillation can be calculated by appropriate formulæ (Glashan, *Phil. Mag.* [iv], **45**, 373), provided only that we know the relation between the composition of the boiling liquid and that of the vapour given off.

In practice the stage through which the process of distillation is passing is recognised by the temperature of the vapour evolved, such temperature being of course always the same for the same mixture at the same pressure.

To sum up, therefore, the equation which represents the relation between the composition of the liquid and that of the vapour given off by it, at a given pressure, together with that which represents the relation between the composition of the liquid and its boiling point at the same pressure, contain all the experimental data which can be derived from the distillation, and form, together with the formulæ above mentioned, a complete history of it. Finally, if we can refer these relations to known laws, we shall have arrived at an explanation of fractional distillation.

The simultaneous distillation of two or more substances varies greatly in character, according to the extent to which they are mutually soluble, and is also influenced by any tendency to combination as in the case of the formation of hydrates; we may therefore consider the subject under four heads as follows:—

(1.) Substances which are not miscible one with the other.

(2.) Substances which mix in all proportions and between which no combination of any kind is known to take place.

(3.) Substances which are mutually soluble to a limited extent only and without combination.

(4.) Substances which are mutually soluble and which combine together to form more or less stable compounds which may be broken up by the process of distillation.

Substances which are not Miscible one with the other.

The experiments of Magnus (*Pogg. Ann.*, **38**, 488) and of Regnault (*Inst. de France*, **26**, 719), have proved that the vapour-tension at a given temperature of a mixture of two liquids which are not mutually soluble is equal to the sum of the vapour-tensions of the two substances separately at the same temperature; the vapour-tension and consequently the boiling point is therefore independent of the proportions in which the two substances are mixed. Applying this law to the distillation of a mixture of the two liquids at a given pressure, we see that it will distil constantly at that temperature at which the sum of their respective vapour-tensions is equal to that pressure. Regnault (*loc. cit.*) found that the boiling point was rather higher than that derived from the vapour-tensions, but attributed the difference to the irregularity which characterises the ebullition of two liquids the one lying above the other. Pierre and Puchot (*Compt. rend.*, **73**, 599, and **74**, 224) state that mixtures of amyl alcohol, of butyl alcohol, of butyl iodide, and of ethyl iodide with water boil at constant temperatures, but whether at these temperatures the sum of the vapour-tensions is equal to the atmospheric pressure cannot at present be ascertained, since as far as I know the vapour-tensions of these sub-

stances have never been measured. (The observations of Regnault on the vapour-tension of ethyl iodide only extend to 50°, whereas the constant boiling point attributed by Pierre and Puchot to a mixture of the iodide and water is 66°.)

A. Naumann (*Deut. Chem. Ges. Ber.*, **10**, 1421, 1819, 2014, 2099) has shown that when a substance which does not mix with water is distilled with steam, the whole passes over at the same temperature; for instance, benzene distils with steam at 69·1°, toluene at 84°, and carbon tetrachloride at 66·7°. At 69·1° the vapour-tension of water is 224·2 mm., that of benzene 533·7 mm., making together 757·9 mm.; at 84° the sum of the vapour-tensions of toluene and water is 747 mm.; while at 66·7° the sum of the vapour-tensions of carbon tetrachloride and water is 762 mm.; the pressures at which the several distillations were made were 742, 752, and 747 mm. respectively. Having regard to the fact that the temperatures are liable to slight variations according to the arrangement of the apparatus, the volume of steam, &c., and that a very small rise of temperature causes a considerable increase in the vapour-tension, it must be allowed that these experiments not only prove with certainty that a mixture of two liquids not mutually soluble has a constant boiling point, but also show that the boiling point is that temperature at which the sum of the vapour-tensions is equal to the pressure at which ebullition takes place. Such, then, is the relation between the composition of the liquid and its boiling point, and such its explanation.

The main result of Naumann's experiments was to show that the ratio of the molecules of the two liquids in the distillate is constant and equal to that of their vapour-tensions at the temperature of distillation; this he conclusively proved, and his observations are supported by those of Pierre and Puchot (*loc. cit.*), who found that the distillate in the case of the iodides and alcohols above mentioned always contained the two substances in the same proportion. Like the boiling point, therefore, the composition of the vapour given off is independent of that of the boiling liquid, and is referable to the vapour-tensions of the two liquids. We have accordingly, as shown on page 549, a complete account of the distillation of this first class of mixtures.

Substances which mix in all Proportions and between which no Combination of any kind is known to take place.

It was after reading the account of Naumann's experiments above referred to that I determined to investigate the distillation of this class of mixtures, and to see if it could not also be referred to the vapour-tensions; the problem is evidently far more complicated, for

neither the boiling point nor the composition of the vapour remains constant during the distillation, nor do the observations of Magnus and Regnault point to any kind of relation between the vapour-tensions of such mixtures and those of their component substances. For my first experiments I selected a mixture of benzene and carbon disulphide, and that for several reasons; firstly, because there is no reason whatever to suppose that these substances have any chemical affinity the one for the other; secondly, because they differ widely in density, and consequently the relative proportions of the two bodies in any mixture could be readily determined by observing its density; thirdly, because they are both obtained pure without much difficulty, and may be easily dried by shaking with sulphuric acid; fourthly, because their molecular weights are nearly equal, the one being 76, the other 78; the vapour-densities, therefore, are also almost equal. The benzene used throughout was purchased of Kahlbaum in Berlin, and was termed "crystallised benzene;" it was afterwards repeatedly digested with sulphuric acid, recrystallised, and distilled from sodium; the whole distilled over between 80·2° and 80·5° (uncorr.); its density was ·88034 at 19·80°, referred to water at the same temperature. The carbon disulphide employed was the ordinary commercial article, well agitated first with mercury, and then with sulphuric acid, and finally subjected to fractional distillation; the whole passed over between 46·2° and 46·5°; its density was 1·26642 at 19·80° referred as before to water at the same temperature.

The relative weights of the two liquids in any mixture were determined by measuring its density; this was done in a **U**-tube, similar to that advocated by Dr. Sprengel, but used in the manner described by me in a paper on the Physical Properties of Homologues and Isomers (*Proc. Roy. Soc.*, **26**, 241). All the densities were taken at very nearly 19·80°; this was very easily done by surrounding the beaker containing the water, in which the tube was plunged by a double copper jacket also containing water; the jacket was about 10 mm. distant from the beaker both at the sides and at the bottom. The tubes having been filled and placed in the beaker, a jet of steam was turned into the water of the jacket until the temperature rose to 20° or 21°; the steam was then allowed to condense in the beaker itself until a thermometer placed in it marked 19·80° as nearly as possible (the same thermometer was used throughout the experiments). During the ensuing 15 minutes, while the tubes were allowed to remain in the beaker, the water of which was continuonsly stirred by means of an electromotor, the temperature remained practically constant, never varying more than a few hundredths of a degree. The densities were finally reduced to 19·80° exactly, on the supposition that the decrease in density of all the mixtures from 19° to 21° was equal to the mean

decrease in density of benzene and carbon disulphide between those temperatures. As the expansions of the two substances are very nearly alike and the correction was always very small, this approximate method of reduction is amply sufficient. All the densities given below are referred to water at 19·80°.

Carbon disulphide is so extremely volatile that exposure to the air very soon materially alters the relative amount of it present in a mixture. While filling the density tubes, this source of error was avoided by having a tube about four inches long by half an inch wide, provided with a small hole near the closed end; the liquid was rapidly poured into this tube, the small hole being stopped with the finger. A cork was then placed in the open end, and the tube held horizontally, while the liquid was sucked into the density tube, the capillary end of which was inserted into the little hole.

With regard to this method of finding the composition of the mixtures, it was not certain that benzene and carbon disulphide would mix without change of volume. In order to see if they did so, I measured the densities of various mixtures containing different proportions of the two liquids. The following table gives the results:—

Percentage of CS_2 in mixture (by weight).	Percentage of CS_2 in mixture (in mols.).	Calculated density at 19·80°.	Observed density cor. to 19·80°.	$\frac{d}{D}$
0·000	0·000	0·88034	0·88034	1·00090
12·634	12·923	0·91561	0·91307	1·00278
24·926	25·415	0·95274	0·94744	1·00559
39·419	40·041	1·00059	0·99354	1·00710
40·961	41·5907	1·00596	0·998676	1·00729
50·388	51·037	1·04012	1·03126	1·00859
61·020	61·636	1·08153	1·07250	1·00842
65·387	65·973	1·09952	1·09132	1·00751
72·463	72·978	1·12996	1·12241	1·00673
79·805	80·220	1·16338	1·15700	1·00552
82·799	83·165	1·17758	1·17184	1·00490
94·673	94·802	1·23751	1·23459	1·00236
100·000	100·000	1·26642	1·26642	1·00000

The fifth column gives the ratio of the calculated density d to the observed D, or, in other words, the volume occupied by a quantity of the mixed liquids which, when they were separate, occupied the unit of volume. It will be observed that the liquids in question expand on mixing, and that the greatest expansion occurs when the molecules of each are present in the mixture in about equal numbers. Taking the percentages of CS_2 in molecules as abscissæ, the corresponding values of

$\frac{d}{D}$ as ordinates a curve was drawn, from which the values of $\frac{d}{D}$ for every 5 per cent. of CS_2 were measured; the theoretical density d having been calculated for the same percentage, the true densities D were obtained by dividing d by $\frac{d}{D}$. By this means the errors resulting from the process of interpolation were reduced as far as possible. A table of the percentages of CS_2 (in molecules) and the corresponding actual densities having been made, the experiments on distillation could be proceeded with. I do not dwell further on this question of the expansion which takes place when benzene and carbon bisulphide are mixed together, as I hope to make it and other similar cases the subject of a future paper.

We have now to find at what temperature any mixture of these two liquids will boil at the ordinary atmospheric pressure, and what will be the composition of the vapour evolved. This can readily be done by distilling various mixtures, collecting the distillates in fractions, and observing their weights and percentage compositions. I may here remark that whenever in the following account mention is made of "percentage of CS_2," the number of *molecules* of CS_2 in 100 molecules of the mixture is always referred to, it being, of course, assumed that the molecules are separate and not grouped together. Any other hypothesis would evidently not be susceptible of exact definition.

If W = weight of liquid placed in the still,
M = percentage of CS_2 in this liquid,
w = weight of first fraction collected,
m = percentage of CS_2 in the fraction,
W_1 = weight of liquid in the still at the moment when the first fraction is removed,
M_1 = percentage of CS_2 in the same liquid,

Then $W_1 = W - w$,

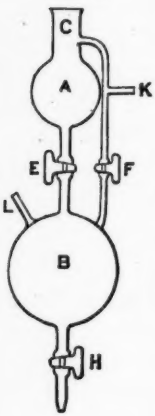
$$\text{and } M_1 = \frac{WM - wm\frac{7800 - 2M}{7800 - 2m}}{W - w\frac{7800 - 2M}{7800 - 2m}}$$

By these equations therefore we know the weight and composition of the boiling liquid at the moment of removal of each successive fraction, and we can observe the boiling point at the same moment. By taking the percentages of CS_2 as abscissæ the temperatures at which ebullition takes place as ordinates, we obtain a number of points which, when sufficient have been accumulated, may be united by a curve, which will express the required relation between the percentage and the boiling point.

If the weight of liquid in the still be large compared with that of a fraction we may assume without appreciable error that, during the distillation of the fraction, the composition of the liquid in the still was constant and equal to the arithmetical mean of the percentages at the beginning and end of that period. Taking these mean percentages of CS_2 as abscissæ, and the corresponding percentages in the successive fractions as ordinates, we determine the positions of a number of points, by uniting which we shall obtain the curve expressing the relations between the composition of the boiling liquid and that of the vapour given off.

For the first distillation a retort, having a capacity of about 750 c.c., was employed. I selected this form of still, as it appeared to subject the vapour to the least chance of condensation before it reached the condenser. The retort was connected with an ordinary Liebig's condenser, to the end of which was adapted a receiver consisting of two bulbs A and B (Fig. 1), communicating with each other by means of a tube provided with a tap E, the end of the condenser was fitted air tight into the wide tube C; from C a small tube with tap F passes to the upper portion of the bulb B; at the bottom of B is a tap H, whence the distillate is withdrawn. During distillation the tap E was open while H was closed, when a fraction of the distillate was to be removed E was closed, and the liquid in B then drawn off at H. This form of receiver was used, in order to avoid evaporation and consequent change of composition of the fractions; it was, however, constructed with a view to distillation at other pressures than that of the atmosphere; in this case the tube K communicates with a reservoir, in which the required pressure is maintained, while the tube L is closed by an india-rubber cap. To withdraw a fraction E and F are closed, thus cutting off B from the rest of the distilling apparatus, the cap at L is then removed to allow the liquid to run out when the tap H is opened.

Fig. 1.



531·3 grams of a mixture, having a density of 1·07430, and therefore containing 61·95 per cent. of CS_2 (by the table of densities and percentages referred to on page 553), were placed in the retort and distilled; the barometric pressure* during the distillation was 772·19 m.m.

The following table gives the details of the distillation, the figures

* The barometric pressure was always measured by means of a standard barometer which had been compared at Kew Observatory; the heights given are corrected for the error of the instrument as thus obtained, and are reduced to 0°.

in column I give the temperatures, between which the several fractions passed over; II, the weights of the fractions; III, their densities reduced to 19·80°; IV, the percentage of CS_2 in the same fractions.

The sum of the numbers in II is 520·09, showing a loss of 11·2 grams during distillation.

TABLE I.

	I.	II.	III.	IV.
I	52·5—54·0°	30·43	1·17064	82·94
II	54·0—55·0	87·38	1·16204	81·24
III	55·0—56·0	64·82	1·15013	78·83
IV	56·0—58·0	82·43	1·13345	75·36
V	58·0—60·0	51·81	1·11001	70·26
VI	60·0—63·0	46·51	1·08300	64·05
VII	63·0—66·0	30·73	1·05219	56·44
VIII	66·0—70·0	32·71	1·01284	45·76
IX	70·0—75·0	29·32	0·96337	30·56
X	75·0—78·0	20·56	0·91875	15·05
XI	78·0—79·7	23·37	0·89347	5·32
XII	79·7—80·0	20·02	0·88261	0·92

In column I of Table II the percentage of CS_2 in the liquid remaining in the retort at the moment of removal of each successive fraction is given (obtained by means of the equations on page 553). II gives the temperatures at which ebullition was taking place at the same moments, the first eight fractions only are taken into account, as the quantity of liquid distilled was small, and the numbers become therefore very uncertain towards the end:—

TABLE II.

I.	II.	I.	II.
61·95	52·5	38·60	60·0
60·67	54·0	31·49	63·0
56·29	55·0	25·86	66·0
52·07	56·0	19·59	70·0
44·80	58·0	—	—

Table III gives in column I the mean percentage composition of the liquid in the retort during the distillation of each fraction; in II the composition of the fraction distilled, or in other words the mean volume per cent. occupied by the carbon disulphide in the vapour given off.

Table III.

I.	II.	I.	II.
61·31	82·94	41·70	70·26
58·48	81·24	35·05	64·05
54·18	78·83	28·67	56·44
48·43	75·36	22·73	45·76

A second distillation was made in a common flask fitted with a short T-piece, such as is ordinarily used in the laboratory. The capacity of the flask was 840 c.c. The same condenser and receiver were used as before both in this and all subsequent distillations. 582 grams of a mixture, of which the density was 1·07352, and which contained therefore 61·76 per cent. of CS_2, were distilled; the barometric pressure during the distillation was 763·7. The following three tables give as in the first case the details and results of the experiment:—

Table IV.

	I.	II.	III.	IV.
I	52·0—54·0°	40·79	1·17733	84·26
II	54·0—55·0	86·99	1·16817	82·45
III	55·0—56·5	84·67	1·15490	79·82
IV	56·5—58·0	65·60	1·13767	76·24
V	58·0—60·0	51·06	1·12019	72·48
VI	60·0—63·0	51·46	1·09427	66·67
VII	63·0—66·0	38·80	1·06280	59·14
VIII	66·0—70·0	37·13	1·02606	49·50
IX	70·0—75·0	36·35	0·97360	33·85
X	75·0—78·5	29·14	0·92213	16·27
XI	78·5—80·0	27·95	0·89149	4·53
XII	80·0—80·2	22·12	0·88149	0·46

Table V.

I.	II.	I.	II.
61·76	52·0	38·80	60·0
60·05	54·0	31·61	63·0
55·73	55·0	25·81	66·0
50·17	56·5	18·96	70·0
44·50	58·0	—	—

Table VI.

I.	II.	I.	II.
60·90	84·26	41·65	72·48
57·89	82·45	35·20	66·67
52·95	79·82	28·71	59·14
47·33	76·24	22·38	49·50

In the third distillation a flask of which the capacity was 1,500 c.c. was used. The neck was cut off, and the **T**-tube pushed well into the flask as drawn (fig. 2). I thought by this arrangement to shield the vapour from the influence of radiation. 992·2 grams of a mixture having a density of 1·11278, and containing, therefore, 70·86 per cent. of CS_2, were distilled. The first eight fractions only were collected. The barometric pressure during the distillation was 757·1 The tables give the results as before.

FIG. 2.

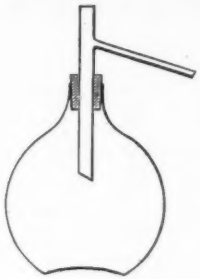


TABLE VII.

	I.	II.	III.	IV.
I	51·0 —51·2°	53·70	1·19866	88·27
II	51·2 —51·55	59·50	1·19375	87·36
III	51·55—51·75	50·10	1·18961	86·58
IV	51·75—52·00	38·60	1·18764	86·22
V	52·00—52·20	50·80	1·18529	85·79
VI	52·20—52·50	63·50	1·18147	85·08
VII	52·50—52·90	50·25	1·17748	84·29
VIII	52·90—53·30	51·90	1·17283	83·37

TABLE VIII.

I.	II.	I.	II.
70·86	51·00	65·35	52·20
69·86	51·20	63·49	52·50
68·67	51·55	61·81	52·90
67·58	51·75	59·84	53·30
66·67	52·00		

TABLE IX.

I.	II.	I.	II.
70·36	88·27	66·01	85·79
69·26	87·36	64·42	85·08
68·12	86·58	62·65	84·29
67·12	86·22	60·83	83·37

The density of the liquid which remained in the still was 1·06598, corresponding to 59·95 per cent. of CS_2; the percentage calculated from the weights and densities of the eight fractions was 59·84 (see Table VIII). This affords a convincing proof of the accuracy of the methods employed.

772·8 grams of a mixture, of which the density was 0·99603, and which contained therefore 40·81 per cent. of CS_2, were now distilled

from the same flask, the barometric pressure being 750·5. The results are given as before.

Table X.

	I.	II.	III.	IV.
I	56·0—59·0°	51·80	1·11241	70·78
II	59·0—59·6	45·05	1·10158	68·35
III	59·6—60·4	47·28	1·09382	66·57
IV	60·4—61·0	30·94	1·08626	64·84
V	61·0—61·8	38·07	1·07952	63·21
VI	61·8—62·8	42·94	1·07135	61·24
VII	62·8—63·8	35·01	1·06024	58·49
VIII	63·8—64·8	32·38	1·04833	55·46

Table XI.

I.	II.	I.	II.
40·81	56·0	30·69	61·8
38·64	59·0	28·13	62·8
36·64	59·6	25·91	63·8
34·37	60·4	23·76	64·8
32·78	61·0	—	—

Table XII.

I.	II.	I.	II.
39·72	70·78	31·73	63·21
37·64	68·35	29·41	61·24
35·50	66·57	27·02	58·49
33·57	64·84	24·83	55·46

The density of the mixture remaining in the flask was 0·94172, corresponding to 23·25 per cent. of CS_2.

910·6 grams of a mixture having a density of 0·92781, and containing, therefore, 18·33 per cent. of CS_2, were distilled from the same flask. The barometric pressure was 752·6. The resulting numbers are given in the following three tables:—

Table XIII.

	I.	II.	III.	IV.
I	66·2 —68·2°	41·11	1·02034	47·88
II	68·2 —68·95	35·21	1·00527	43·55
III	68·95—69·3	22·16	·99968	41·90
IV	69·3 —69·8	25·63	·99508	40·53
V	69·8 —70·2	22·72	·99132	39·39
VI	70·2 —70·6	21·91	·98669	37·96
VII	70·6 —71·0	20·38	·98217	36·55
VIII	71·0 —71·5	24·90	·97756	35·02
IX	71·5 —72·0	24·50	·97240	33·47
X	72·0 —72·4	22·47	·96849	32·21

TABLE XIV.

I.	II.	I.	II.
18·33	66·2	12·76	70·6
16·92	68·2	12·08	71·0
15·79	68·95	11·26	71·5
15·07	69·3	10·44	72·0
14·24	69·8	9·69	72·4
13·48	70·2	—	—

TABLE XV.

I.	II.	I.	II.
17·63	47·88	13·12	37·96
16·36	43·55	12·42	36·55
15·43	41·90	11·67	35·02
14·65	40·53	10·85	33·47
13·86	39·39	10·06	32·21

The mixture remaining in the flask had a density of 0·90401, corresponding to 9·47 per cent. of CS_2.

601·84 grams of a mixture having a density of 0·90382, and containing, therefore, 9·44 per cent. of CS_2, were now distilled with the same apparatus. The barometric pressure during the experiment was 735·8. Tables XVI, XVII, and XVIII give the results as in the above cases.

TABLE XVI.

	I.	II.	III.	IV.
I	70·6—72·6°	33·36	·96014	29·50
II	72·6—73·6	30·14	·94489	24·36
III	73·6—74·1	26·45	·93723	21·68
IV	74·1—74·6	22·64	·93208	19·87
V	74·6—75·0	22·08	·92706	18·06
VI	75·0—75·5	24·18	·92299	16·58
VII	75·5—75·9	21·39	·91833	14·89
VIII	75·9—76·3	21·15	·91380	13·18
IX	76·3—76·6	19·07	·91014	11·80
X	76·6—77·0	22·83	·90652	10·43

TABLE XVII.

I.	II.	I.	II.
9·44	70·6	4·81	75·5
8·26	72·6	4·30	75·9
7·35	73·6	3·83	76·3
6·61	74·1	3·43	76·6
5·99	74·6	2·98	77·0
5·42	75·0	—	—

TABLE XVIII.

I.	II.	I.	II.
8·85	29·50	5·11	16·58
7·80	24·36	4·55	14·89
6·98	21·68	4·06	13·18
6·30	19·87	3·63	11·80
5·70	18·06	3·20	10·43

The density of the liquid remaining in the flask was 0·88678. It contained, therefore, 2·62 per cent. of CS_2, while the calculated percentage is 2·98.

The various boiling points and corresponding percentages as given in Tables II, V, VIII, XI, XIV, and XVII were expressed geometrically in the usual manner, the percentages being measured horizontally, on the scale of 1 inch = 5 per cent., the boiling points vertically, on the scale of 1 inch = 10 degrees.

A curve was then drawn as the locus of the points thus obtained; tho whole of the points lie fairly on this curve, except those given by the last distillation (Table XVII), which are a little below. This I attribute to the low reading of the barometer at the time of the distillation. To have really comparable results the boiling point ought of course to be reduced to 760 mm. This, however, cannot be done correctly, as the variation of the boiling points with the pressure for mixtures of CS_2 and C_6H_6 is unknown. (My friend Mr. Gaskell and myself are now engaged in measuring the vapour-tensions of these mixtures.) Such correction would moreover in this case be superfluous, as the results are slightly uncertain, owing to the cooling to which the vapour is subjected in the upper part of the flask.

(The first two distillations were made with too small a quantity of liquid to give reliable results for this curve.)

From the data furnished by Tables IX, XII, XV, and XVIII, a second curve was drawn, the percentages of the mixtures being as before represented, horizontally on the scale of 1 inch = 5 per cent., the percentages of the evolved vapour vertically on the scale of 1 inch = 10 per cent. All the points lie very near the curve, but some of the series are either a little above or a little below it. An uncertainty of about 0·1 inch or 1 per cent. thus results in the position of the curve; this also is probably caused by the cooling of the vapour in the flask, a source of error which will be carefully and completely avoided in future experiments.

The second and third columns of the following table give respectively the boiling points of, and percentages of CS_2, in the vapour evolved by the various mixtures, of which the percentage composition

is given in the first column. These three columns, therefore, sum up the results of the experiments detailed above.

Per cent. of CS_2 in mixture.	Boiling point.	Per cent. of CS_2 in vapour evolved.	Ratio of molecules in mixture.	Ratio of vapour tensions at boiling point.	Product of ratios.	Corresponding percentage.	Percentage obtained by multiplying by 3·8.
0	80·2°	0·0	0·000	2·7008	0·0000	0·00	0·00
5	76·2	18·0	0·053	2·7519	0·1459	12·73	16·8
10	72·5	30·6	0·011	2·8013	0·3109	23·72	29·7
15	69·4	40·7	0·176	2·8439	0·5005	33·36	40·1
20	66·6	48·7	0·250	2·8845	0·7211	41·90	48·7
25	64·2	55·4	0·333	—	—	—	—
30	62·2	61·2	0·429	2·9511	1·2660	55·87	62·0
35	60·4	66·3	0·538	—	—	—	—
40	58·8	70·7	0·667	3·0053	2·0045	66·72	71·7
45	57·3	74·4	0·818	—	—	—	—
50	55·7	77·7	1·000	3·0568	3·0568	75·35	79·2
55	54·3	80·2	1·222	—	—	—	—
60	53·0	82·9	1·500	3·1043	4·6565	82·32	85·1
65	51·9	85·3	1·857	—	—	—	—
70	50·9	87·7	2·333	3·1421	7·3305	88·00	89·9
75	50·0	89·8	3·000	—	—	—	—
80	49·2	91·8	4·000	3·1741	12·6964	92·70	93·8
85	48·4	93·8	5·667	—	—	—	—
90	47·8	95·9	9·000	3·2014	28·8126	96·65	97·2
95	47·2	97·9	19·000	—	—	—	—
100	46·6	100·0	∞	3·2248	∞	100·00	100·0

With regard to the explanation of the numbers in the third column, the most probable hypothesis is that the ratio of the volume of CS_2 to the volume of C_6H_6 in the vapour evolved by equal numbers of molecules of the two liquids is equal to the ratio of their vapour-tensions at the temperature of ebullition of the mixture. Were this the case, the product of the ratio of the numbers of the molecules of CS_2 and C_6H_6 in the mixture by the ratio of the vapour-tensions at the boiling points of the mixture would be equal to the ratio of the volumes of the substances in the vapour evolved. The fourth, fifth, and sixth columns of the table give those ratios and their products, the seventh column gives the percentage of CS_2 corresponding to the ratios in the sixth column. It is seen that these percentages are not equal to those obtained from the curve representing those experiments, and given in the third column. If, however, the numbers in the fourth column be multiplied by the constant quantity 3·8, instead of the varying ratios given in the fifth column, the percentages are obtained as given in the

eighth column of the table; these numbers are approximately equal to those in the third column.

It would appear, therefore, that when a mixture of carbon disulphide and benzene is heated to boiling, the vapour which is given off contains the two substances in such relative quantities that the ratio of their volumes is equal to the ratio of the numbers of their molecules in the mixture multiplied by the quantity 3·8. In other words, whatever may be the mixture, a quantity of carbon disulphide containing a certain number of molecules will evolve 3·8 times as much vapour as a quantity of benzene containing an equal number of molecules.

The meaning of this particular number 3·8 can only be sought for when similar experiments have been made with other mixtures.

LX.—*Transformation of Aurin into Triphenylpararosaniline.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

In our last paper (this Journal, 1879, 148), we stated that we hoped to get hold of the intermediate products undoubtedly existing between aurin and pararosaniline. But so far we have not had much success, although varying both the quantity of ammonia and the temperature. In some cases little or no action had taken place, whilst in others a large quantity of pararosaniline was formed, even on using only one molecule of ammonia to one of aurin.

As we encountered such difficulties with ammonia, we tried the action of methylamine, and found that an aqueous solution of this base acts readily on aurin at 125°, and transforms it almost entirely into a purple colour possessing all the properties of a trimethylrosaniline: $C_{19}H_{14}O_3 + 3(CH_3)NH_2 = C_{19}H_{14}(CH_3)_3N_3 + 3H_2O$.

At the same time intermediate compounds soluble in alkalis are formed, and these are obtained in quantity by heating the mixture only to 100°. Our first attempts to isolate these failed completely, as the alkaline dark-red solution, when exposed to the air for only a short time, turned brown, and colourless needles were deposited. Caustic potash, ammonia, and other alkalis act on aurin under certain conditions in the same way; it is therefore necessary, in order to avoid this change, to pour the contents of the tubes, after opening, at once into an excess of dilute hydrochloric acid.

Trimethylamine acts also readily on aurin, converting it into purple colouring matters. All these compounds are under investigation, and we will only add that our researches have shown that almost all the so-called aniline colours can be obtained from phenol.

LXI.—*On the Boiling Points of certain Metals and Metallic Salts.*

By Thos. Carnelley, D.Sc., and W. Carleton Williams, Assistant Lecturers on Chemistry, Owens College.

In a former communication (*Jour. Chem. Soc.*, 1878, **1**, 281) we described a simple method of measuring the temperature of ebullition of those bodies whose boiling points are beyond the range of the mercurial thermometer, viz., by ascertaining whether certain salts, the melting points of which are known (*ibid.*, 1878, 273—281), melt on exposure to the vapour of the boiling substance.

By slight modifications in this method we have been able to determine the boiling points of several elementary and compound bodies. The results obtained are given in the following table. Column I contains the name of the substance; II, the salts used in determining the boiling point, the symbol + being used to indicate that the salt melts, and − to show that fusion does not take place; III, gives the melting points of the salts; IV, the boiling points of the substance:—

I.	II.	III.	IV.	Remarks.
Palmitic acid ..	+ KNO_3	339°	(339—359)	Obtained pure from Trommsdorff. M. p. = 60·5° (62°) Fittig. B. p. as determined by a Geissler's mercurial thermometer = 348° (corr.). Boiled with little or no decomposition.
	− $KClO_3$	359		
Stearic acid....	+ KNO_3	339	(359—383)	Obtained pure from Trommsdorff. M. p. = 69° (69·2°) Pebal. Boiled with little or no decomposition.
	+ $KClO_3$	359		
	− PbI_2	383		
Selenium.....	+ V_2O_5	658	(676—683)	Boils somewhat below 700°. M. p. = 217° (Hittorf, *Jahrb.*, **4**, 319).
	+ $CaBr_2$	676		
	− RbBr	683		
	− Li_2CO_3	695		
Tellurium dichloride	—	—	327 (corr.)	By mercurial thermometer.
Tellurium tetrachloride	+ $Tl_{12}V_{10}O_{31}$	404	414	Prepared by heating Te in excess of chlorine gas.
	+ $Tl_{12}V_{14}O_{41}$	408		
	$Ba(ClO_3)_2$	half melts 414		
	− TlCl	427		
Tellurium tetrabromide	+ $Tl_{12}V_{14}O_{41}$	408	(414—427)	Prepared by heating Te in excess of bromine vapour.
	+ $Ba(ClO_3)_2$	414		
	− TlCl	427		
	− AgCl	451		
Stannous chloride	+ $Ag_4P_2O_7$	585	(617—628)	Prepared by passing a current of HCl gas over the molten metal. M. p. = 249·3° (corr.) = 250° (*Watts's Dict.*).
	+ $NaPO_3$	617		
	− NaI	628		
	− $SrBr_2$	630		

I.	II.	III.	IV.	Remarks.
Stannous bromide	+ $NaPO_3$	617°	(617°—634°)	Prepared by distilling a mixture of Sn and $HgBr_2$. M. p. = 259° (corr.). Another preparation boiled 632—634°.
	− Tl_2SO_4	632		
	− KI	634		
Stannous iodide decomposes rapidly on boiling				Obtained by precipitating $SnCl_2$ with KI in red needles. M. p. = 316°. The text-books state that it is volatile at a red heat.

The highest melting point given in the list of salts already referred to is that of Na_2SO_4, melting point 861°, so that in order to obtain approximately the temperature of the vapour of bodies boiling above 861°, we have been obliged to make use of the melting points of certain pure metals, viz., Ag, Cu, Ni, and wrought-iron (piano wire). The temperatures at which these metals melt have been determined by several authorities, with the following results :—

Silver .... 1034° C., Guyton Morveau (*Watts's Dict.*).
1000 Pouillet (*Watts's Dict.*).
999 Prinseps (*Phil. Trans.*, 1828, 94).
1024 Daniell („ „ 1830, 237).
954 Violle (*Compt. rend.*, **85**, 543).
1040 Riemsdyk (*Chem. News*, **20**, 32).
1023 Plattner.
916 Deville.

Copper .... 1000—1200° C., Pouillet (*Watts's Dict.*).
1207° C., Guyton Morveau („ „).
1330 Riemsdyk (*Chem. News*, **20**, 32).
1090 Daniell (*Phil. Trans.*, 1830, 237).
1236 Wilson (*Fortsch. d. Phys.*, **8**, 425).
1050 *Mott's Chemist's Manual.*

Nickel .... 1600 Van de Weyde (*Dict. of Mechanics*).

Iron (wrought) 1800° C., Van de Weyde (*Dict. of Mechanics*).
1600 Pictet (*Compt. rend.*, **88**, 1317).

By the use of these metals, the following boiling points were determined :—

I.	II.	III.	IV.	Remarks.
Lead chloride..	+ Na_2SO_4	861°	(861°—1000)	Prepared by precipitation.
	− Ag	1000		
Cadmium chloride	+ Na_2SO_4	861		
	− Ag	1000		

Glass tubes are rapidly corroded by molten potassium and sodium, and could not be used in determining these boiling points. The metals

were therefore distilled in a wrought-iron tube, the lower half of which was heated in a coke furnace. The air in the tube was displaced by a current of coal-gas, to prevent oxidation of the boiling metal; both metals boiled with great regularity, much more so in fact than had been expected. The salts or metals used in the determinations were exposed to the potassium or sodium vapour in long capillary tubes of hard glass. These tubes were externally corroded by the metallic vapours, though not to such an extent as to eat through the glass.

I.	II.	III.	IV.	Remarks.
Sodium	+ Na_2CO_3	814°	(861—1000°)	That portion of the iron tube which was in contact with the vapour was at a full red heat. The Na vapour has a violet colour.
	+ Na_2SO_4	861		
	− Ag	1000		
Potassium	+ $CaCl_2$	719	(719—731)	The iron tube in contact with the vapour was at a dull red heat.
	$-2(Pb_2V_2O_7)PbO$	731		
	− KCl	734		
	− NaCl	772		

When the temperature of the boiling substance is above 1000°, glass capillary tubes can no longer be used for containing the metals to be exposed to its vapour, in which case the metals employed in measuring the boiling point are enclosed in a small thin iron cylinder, the open end of which is closed with a tight-fitting plug of the same metal. This is lowered into the boiling liquid or vapour by an iron wire, where it is allowed to remain for five minutes. In this way the following boiling points were determined:—

I.	II	III.	IV.	Remarks.
Bismuth	+ Ag	1000°	(1090—1450°)	
	+ Cu	1090		
	− Ni	1450		
Lead (pure) ..	+ Cu	1090	(1600—1600)	The pure metal boils at a white heat. A sample of common lead boiled between the m. p.'s of Cu and Ni.
	+ Ni	1450		
	− Fe	1600		

As tin and antimony rapidly alloy with iron, they cannot be boiled in iron tubes, but this difficulty is easily overcome by using an apparatus consisting of a Hessian crucible surmounted by an iron cylinder. Instead of an iron case, which was found to be quickly eaten through by boiling tin or antimony, the Ag, Cu, Ni, or Fe is placed in the stem of a tobacco-pipe, care being taken to close the end of the pipe completely, so as to prevent the molten tin or antimony from penetrating to the enclosed metal. This is best done by first inserting the test metal, and afterwards closing the hole with a plug of kaolin, the end of the pipe being finally covered with a glaze, consisting of a mixture of fused borax and kaolin:—

I.	II.	III.	IV.	Remarks.
Tin	+ Ag	1000	(1450—1600)	According to Van de Weyde Sn boils at 1700°. Text-books generally state a white heat.
	+ Cu	1090		
	+ Ni	1450		
	− Fe	1600		
Antimony	+ Cu	1090	(1090—1450)	
	− Ni	1450		

Both the tin and antimony boiled very well; the tin appeared to be more easily volatile than lead.

In all cases no less than two experiments were made as regards the final limits obtained.

Wiebe (*Deut. Chem. Ges. Ber.*, **12**, 788) has recently described a method for calculating the boiling points of elements when their melting points, coefficient of expansion, specific heat, and atomic weight are known, and in all cases (viz., Hg, Cd, Zn, Se, S, P) in which the necessary data were known, the calculated agreed very well with the experimental boiling points. We have now applied Wiebe's method of calculation to the boiling points of Sb, Bi, Pb, and Sn, with the following results:—

	Calculated by Wiebe's Method.	Found.
Sb	1961	1090—1450
Bi	1580	1090—1450
Pb	905	1450—1600
Sn	972	1450—1600

From the above it is seen that the calculated agree fairly well with the experimental boiling points as regards Bi, while for Sn, Pb, and Sb, the contrary is the case.

A curious relation (whether accidental or not it is impossible to say) exists between the melting and boiling points of Cl, Br, and I, and those of S, Se, and Te, for the melting points of S, Se, and Te are respectively twice, and the boiling points three times as high as those of Cl, Br, and I, all being reckoned from the absolute zero (− 273° C.), thus:—

Melting Points.

Cl (Berthelot)....	198 × 2 = 396	S =	388 (Person).
Br (*Watts' Dict.*)	251 × 2 = 502	Se =	490 (Hittorf).
I (Gay-Lussac) ..	380 × 2 = 760	Te =	755 (Authority not known). 773 (*Watts' Dict.*).

Boiling Points.

Cl (Regnault)....	240 × 3 = 720	S =	720 (Regnault, Williams, and Carnelley).

Br	(Löwig)....	318 × 3 = 954	Se =	953	(Williams and Carnelley).
	(Andrews)..	331 × 3 = 993			
I (Stas)		473 × 3 = 1419	Te =	?	

If the above relation holds good also for the boiling point of tellurium, then the latter element should boil at (1419 − 273) = 1146° C.

LXII.—*On Dry Copper-zinc Couples and Analogous Agents.*

By J. H. Gladstone, F.R.S., Ph.D., and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

In the Journal of the Chemical Society (1877, i, 567) we described in detail the mode of procedure for preparing what we have styled "dry couples," in contradistinction to ordinary copper-zinc couples, the latter from their very mode of formation being necessarily associated with water. Briefly, it consists in depositing the metal contained in a certain volume of a 2 per cent. solution of copper sulphate, on a given weight and surface of crumpled zinc foil, washing the conjoined metals with water to remove zinc sulphate, then with alcohol to remove the water, subsequently with ether, and finally heating the metals in a current of hydrogen to remove ether and any traces of water, and to bring about the disintegration of the foil. All this involves time and not inconsiderable trouble, and the necessity of employing expensive liquids as ether and alcohol is a decided disadvantage. Of course, when the object is to study the power of a new agent, or to employ it in the preparation of a valuable body, such considerations are of little moment; still anything which would lighten the labour or lessen the cost attending its use would be deserving of welcome.

Six years ago we pointed out the value of the dry couple in the preparation of zinc-ethyl, and since that time we have shown its applicability to the preparation of other zinc ethers. But our recent success in this direction in obtaining 99 per cent. of the theoretical yield of zinc methyl, which valuable reagent could only be satisfactorily obtained before by the substitution of zinc for mercury in the highly poisonous compound mercuric methide, led us to think of the possibility of simplifying the preparation of the dry couple. More especially did it seem desirable to dispense, if possible, with the use of the ether and alcohol.

It was obvious that these liquids could be dispensed with only by a

radical change in the method of bringing about the mechanical association of the copper and zinc. Our first attempts towards doing this, which consisted in mixing zinc filings with variable amounts of finely divided copper, and subjecting the mixture to pressure in a steel tube, were attended with but very imperfect success. The cause of the practical failure of this method was, however, soon discovered. It was noticed when the cylinders of the compressed metals were struck perpendicularly to their axes, which it was necessary to do in order to reduce them to small pieces, that the contact of the dissimilar metals had been only partially effected. It now occurred to us that this mechanical association which is so absolutely necessary might become more perfect were the metals after compression heated to the point where zinc begins to change its physical condition, and it was thought that in order to prevent oxidation, this heating might advantageously be done in hydrogen gas. The success of the experiments which resulted from the first anticipation was beyond our most sanguine expectations.

The activity of the new couple was ascertained by observing the rate at which 5 c.c. of ethyl iodide was converted into zinc ethiodide. The flasks containing the materials, to which inverted condensers were attached, were heated by immersion in water at 90° C. In each trial 9 grams of zinc filings were used. The amounts of copper, which varied for each experiment, with other particulars, are set out in the annexed table :—

Compressed Metals in Hydrogen.

Expt.	Copper.	Time for conversion into ethiodide.
I....	4·0 grams.	60 minutes.
II....	2·0 „	13 „
III....	1·0 „	8 „
IV....	1·0 „	9 „
V....	0·5 „	8 „
VI....	0·25 „	14 „
VII....	0·125 „	29 „

It results from these experiments that the relative weights of copper in the same physical condition exert a very considerable influence, and that a dry couple, almost equal in activity to the original dry couple, can be prepared in any quantity without the aid of ether or alcohol.

The activity of the several couples bears, no doubt, some close relation to the number of *separate* contacts between the dissimilar metals in each case.

We now experimented with the object of ascertaining the value of the compression. The results obtained without compression given below show that it is of but little importance :—

Non-compressed Metals in Hydrogen.

Expt.	Copper.	Time for conversion into ethiodide.
VIII ..	1·0 gram.	9 minutes.
IX ..	1·0 „	10 „
X ..	0·5 „	12 „
XI ..	0·25 „	19 „

In the hope of still further simplifying the preparation, we experimented with couples prepared without compression, dispensing also with the heating in hydrogen. When the heating was effected in a flask open to the air, the activity of the couples produced was found to be much smaller; but when it was done in a flask provided with a cork through which passed a tube with a capillary opening, which was closed by fusion as soon as the heating was discontinued, the activity of the resulting couples to our astonishment was found to be actually greater than the activity of those prepared in hydrogen. The results of four experiments made in this way at different times are tabulated below :—

Non-compressed Metals in Air.

Expt.	Copper.	Time for conversion into ethiodide.
XII....	1·0 gram.	6·0 minutes.
XIII....	1·0 „	7·5 „
XIV....	1·0 „	7·0 „
XV....	1·0 „	6·0 „

The time required to bring about the conversion of the ethyl iodide by the old dry couple containing very nearly 9 grams of zinc is from six to nine minutes. Our success was therefore complete. Why a small quantity of air should be actually advantageous will be discussed presently.

We now describe in detail the method for preparing the most effective couple.

Place in a dry flask coarse zinc filings and finely divided copper in the proportion of 9 grams of the former to one of the latter, and fit to its mouth a cork bearing a glass tube through it with a capillary ter-

mination. After mixing the metals by shaking, immerse the bulb of the flask, held horizontally, in a moderately hot Bunsen flame. The flask is now so twisted by a jerking motion of the wrist, that the metals are continually thrown over, until the filings just begin to lose their shape and acquire a yellowish tinge, then shake somewhat rapidly first in the flame and afterwards away from it. The heating of the metals in the quantities hitherto employed usually takes from one to two minutes. When the manipulation has been successful, a number of dark grey small granular masses without metallic lustre are obtained. When the heating has not been sufficient the shape of the filings is more or less discernible, and when the heating has been excessive the metals resemble semi-fluid yellowish shot, slightly lustrous in appearance. This latter condition, in which in all probability the metals are chemically associated in an alloy, is absolutely fatal. The phenomena, however, which accompany its production being so marked, enable the operator, after a very little experience, to distinguish it readily from the true "couple condition."

Condition of the Metals employed.

Zinc.—The zinc used in these experiments was in coarse filings, made from ordinary commercial sheet zinc by a zinc worker's coarse single cut file.

Copper.—The copper first used was precipitated by zinc from a moderately strong solution of its sulphate, then thoroughly washed with water, dried and heated in a current of hydrogen. It was in a fairly fine state of division, and light chocolate in colour.

As might be expected, the state of division of the copper is of great importance. Experiments made to obtain definite knowledge on this point showed that when the metal was in comparatively coarse particles, as in very fine filings, the activity of the couple of which it formed part was very much smaller; and when the copper was in as fine a condition as it is possible to obtain it by precipitation from a weak solution of its sulphate, the difficulty of preventing the two metals on heating from passing from the couple to the inactive condition was much augmented, so much so in fact, as to render the operation one requiring extreme care. These facts, conjoined with a knowledge of the labour involved in the preparation of suitable copper by different methods, induce us to recommend that condition of the metal which may be obtained by the reduction of its protoxide at the lowest possible temperature in a current of hydrogen, and sifting the product through fine muslin. Specimens prepared in this way from the powdered black oxide used in combustion analysis, gave couples equal and slightly exceeding in activity the most active ones employed in this inquiry.

Experiment on a Larger Scale.

For the solution of the problem set before us, it has been sufficient to work on a comparatively small scale, but there appears nothing in the nature of any of the operations described to prevent them from being successfully performed on a much larger scale. To remove all doubts on this point, we determined to make an experiment on the preparation of zinc ethyl by our new couple, employing 87 grams of ethyl iodide and a proportionate quantity of couple.

The 90 grams of zinc filings used and the 10 grams of copper (from the oxide) were heated in the manner already described by a somewhat large Bunsen burner, in a 300 c.c. flask. This occupied five minutes. The mechanical association of the metals was not so perfectly effected as it is possible to associate them by heat, which arose from excess of caution. A little experience would be alone required to bring about the complete success of the operation, on whatever scale attempted. The 87 grams of ethyl iodide were now poured into the flask (to which an inverted condenser was attached) containing the couple, and the whole was heated by immersing the lower part of the bulb of the vessel in water at about 90° C. The liquid boiled in a few seconds, in nine minutes a large number of small bubbles appeared, a sure indication of rapid action, and in 15 minutes the conversion into ethiodide was complete. This completion is easily recognised by no more liquid iodide dropping again into the flask from the condenser. The flask was next attached to an ordinary condenser filled with dry hydrogen, and heated in an oil-bath, when at about 160° C., distillation began, which continued for 30 minutes. The zinc ethyl obtained was free from iodide, and weighed 31 grams. The 87 grams of ethyl iodide could produce theoretically 34·3 grams. We have, therefore, obtained 90·4 per cent. of the theoretical amount.

Couples of various Elements.

We have not hesitated in our papers to call the agent which we employ "the copper-zinc couple;" although aware that this has frequently led to misapprehension. The term suggests to many minds the metallic elements of a voltaic battery, and the first impression conveyed has frequently been that we were using a battery of low intensity with its conducting wires, &c. We have, however, purposely retained the term, because we have all along believed that the action was really of the same character as that which takes place in ordinary electrolysis, and indeed was identical with what occurs within the voltaic cell. There are the two metals in contact, standing in the decomposable liquid, only instead of one pair of plates, or several pairs joined together, we have minute pieces of metal, forming myriads of

circuits. There is this great advantage also in our arrangement, that the resistance of the binary compound is reduced to a minimum, as it washes the very points of contact of the metals.

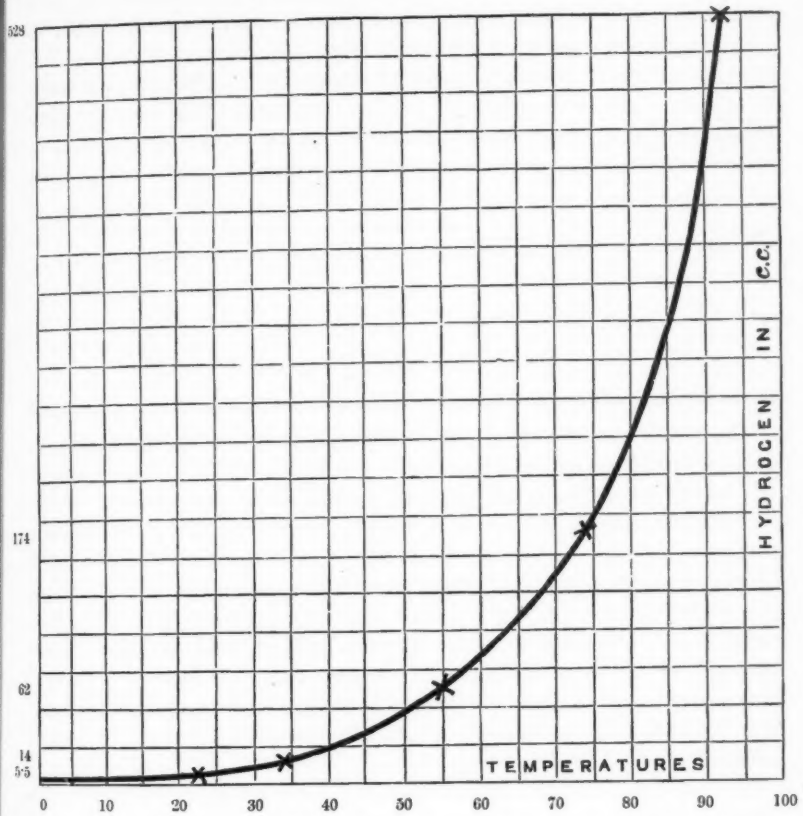
Of course it follows from this view that if we were to employ metals wider apart than copper and zinc in the strength of their chemical affinities, or in other words which give a greater difference of potential, we might expect a more energetic action. Perhaps, too, we should be able to split up compounds which are capable of resisting the couple we have usually employed. Indeed, in our first paper on the subject, we showed that this increased action did not occur: for on employing platinum instead of copper with the zinc, we obtained a much more rapid decomposition of water. From experiments subsequently made and partially communicated to the British Association, it would appear that the power of the copper-zinc couple to decompose water is almost *nil* at 0° C., and very great near the boiling point of the liquid. In fact $1\frac{1}{2}$ metres of zinc foil 5·5 cm. wide, on which copper had been deposited, was placed in pure ice-cold water, and heated by various stages, the amount of hydrogen produced at each stage being ascertained. The results are given in the table below. We have repeated the experiment with the same amount of zinc foil on which platinum was deposited, and obtained the following comparative figures:—

Temp.	Copper-zinc.		Platinum-zinc.	
	Time.	Hydrogen.	Time.	Hydrogen.
2° C. ..	3 hrs.	3·3 c.c.	5 mins.	1·65 c.c.
22 „ ..	2 „	11·1 „	„	7·3 „
34 „ ..	45 mins.	10·4 „	„	8·25 „
55 „ ..	15 „	15·5 „	„	28·0 „
74 „ ..	10 „	29·1 „	„	105·0 „
93 „ ..	5 „	44·0 „	„	150·0 „

These figures calculated for one hour at each temperature, give the following comparison:—

Temp.	Hydrogen per hour.	
	Copper zinc.	Platinum-zinc.
2° C. ..	1·1 c.c.	19·8 c.c.
22 „ ..	5·5 „	87·6 „
34 „ ..	14·0 „	99·0 „
55 „ ..	62·0 „	336·0 „
74 „ ..	174·0 „	1260 0 „
93 „ ..	528·0 „	1800·0 „

The results obtained with the copper-zinc couple give a curve represented in the following diagram:—



This shows clearly that the action is very small, even at the ordinary temperature, but that it becomes very rapid indeed near the boiling point. It would have appeared still more rapid if the action of the couple had not been considerably reduced by this time, through the formation of zinc oxide. This latter action produces a still more serious irregularity in the results with the platinum couple. But it is evident that the more negative metal platinum is capable of inducing considerable effect on water at a temperature at which copper is almost without influence, namely near the freezing point. It is probable also from the experiment, that the superiority of platinum is not maintained in the same proportion at temperatures where both the couples are very effective.

In the experiments just described the quantity of the negative metal

was not determined, but we know from previous work, that the superiority of the platinum is maintained even when its weight is actually less than that of the copper in the comparative experiment, and also that the result is the same with a different positive metal. Thus in some experiments with aluminium couples, communicated to the *Phil. Mag.*, in 1875, in which ·43 gram of copper and ·2246 gram platinum were each deposited upon 6 grams of aluminium foil (126 cm. by 5 cm. wide), results were obtained as in the following table :—

Temp.	Time.	Al-Cu expt. Hydrogen evolved.	Al-Pt expt. Hydrogen evolved.
12° C. ..	22 hrs.	2·5 c.c.	4
100 ..	next 6 „	375 „	484
„ ..	„	92 „	114
„ ..	„	55 „	78
„ ..	„	33 „	45

The formation of a good couple depends, however, on other circumstances than the electromotive force of its elements. One very essential thing is that the negative metal should stick well upon the zinc, and in this respect copper was found to have a great advantage over platinum, silver, or gold. Further, in the making of couples by means of solutions of salts, the more active couple acts itself so rapidly on the water, that the zinc becomes considerably oxidised before the metals are thoroughly washed. It was evident, however, that these objections would not apply to the couples made in the dry way, and it was certainly worth investigation whether a more powerful combination could not be prepared than zinc and copper. The following combinations have been tried :—

Zinc and Silver.—The silver was obtained in a fine crystalline powder by precipitation from the nitrate by means of copper. It was mixed with zinc filings in the manner already described. 9 grams of zinc and 5 c.c. of ethyl iodide were used, with varying proportions of silver. Action took place, and was measured as before.

Expt.	Silver.	Time for conversion into ethiodide.
XVI ..	0·5 gram.	9 minutes.
XVII ..	1·0 „	5 „
XVIII ..	1·0 „	6 „
XIX ..	2·0 „	13 „
XX ..	3·0 „	15 „

It appears, therefore, that a dry couple, consisting of 1 gram of silver

to 9 grams of zinc equals if it does not exceed in strength the best dry copper-zinc couples.

Zinc and Platinum.—The platinum was prepared in fine powder by precipitation with an alkaline formate. It was heated with zinc filings, but before the zinc fairly softened, the two metals combined together with deflagration. Three experiments, however, were made with couples so prepared:—

Expt.	Platinum.	Time for conversion into ethiodide.
XXI ..	1 gram.	18 minutes.
XXII ..	2 „	30 „
XXIII ..	3 „	38 „

This poor result was in all probability due to the fact that the two metals alloyed. We therefore shook up some zinc filings with the platinum, and tried the mixture upon ethyl iodide. It did not act at all at the ordinary temperature during 24 hours, but neither did a similar mixture of finely divided copper and zinc filings. At the boiling point, the mixture of zinc and platinum gave 0·8 per cent. of the total action.

Zinc and Palladium.—Palladium was obtained in a similar manner to the platinum above mentioned, and when heated with zinc filings, deflagrated in the same way. The proportion employed was 1 to 9, and the time required for transforming 5 c.c. of ethyl iodide was 20 minutes (Experiment XXIV).

Zinc and Gold.—Gold was also prepared in the same way. It did not deflagrate with zinc, but from the appearance of the mass under the microscope, it was concluded that the two metals had alloyed. The following times were obtained:—

Expt.	Gold.	Time for conversion into ethiodide.
XXV ..	1 gram.	13 minutes.
XXVI ..	2 „	10 „

Zinc and Carbon.—Cocoa-nut charcoal in powder was employed, but when heated with zinc, the two were found not to stick together; in fact the metal, being much heavier, separates from the mixture. Its action on ethyl iodide was very doubtful.

Zinc and Brass.—It has already been stated that when the zinc filings and copper are heated too strongly together, they combine and

form a couple, which is practically worthless. Under these circumstances the microscope reveals the presence of pieces of yellow brass. Now brass in fine filings was found to have no action whatever on ethyl iodide, even when the experiment was continued for five hours. In the light of the above facts, it seemed possible that brass, if associated with zinc, might render the latter active. On trying the experiment with brass filings mixed with zinc filings, in the proportion of 1 to 9, the conversion of the ethyl iodide took place in 27 minutes (Experiment XXVII). This is a good result when the imperfection of the union of the two metals is considered, in fact copper in similar fine filings mixed with zinc took a longer time to effect the change, which shows that brass must be about as good for the purpose as copper.

Magnesium and Platinum.—As magnesium is reputed to be a more positive metal than zinc, it might be expected to give a more powerful couple with copper or platinum. And so it does, for, as pointed out by one of us (*Proc. Royal Inst.*, 1876), if strips of magnesium foil be coated with finely divided platinum by immersing them in platinic chloride, and the resulting salts be washed away, a couple may be obtained which produces a most vigorous evolution of hydrogen when it is placed even in cold water. On attempting, however, to make dry couples with magnesium, serious difficulties were encountered. The metal is pretty sure to be protected by a coating of oxide, more or less thick, and magnesium does not possess that very convenient property of softening at a moderate heat, and allowing the other metal to sink into its surface, and thus form a perfect connection. Our experiments with dry magnesium, copper, platinum, or carbon-magnesium couples, gave no promising results.

Attention has already been drawn to the circumstance that a dry copper-zinc couple seems to be more powerful when it is prepared in the presence of a small quantity of air. It is known that the copper plates of an old-fashioned voltaic battery are the better for being somewhat oxidated, and Sir W. Thomson finds that the difference of potential between copper and zinc is actually increased by partial oxidation of the former. This led us to try couples in which the suboxide or even the protoxide of copper were the negative elements.

Zinc and Cuprous Oxide.—The dry couples were prepared in the manner described above, but with cuprous oxide obtained by precipitation from copper sulphate by means of glucose. The following were the results:—

Expt.	Cuprous oxide.	Time for conversion into ethiodide.
XXVIII..	0·5 gram.	7·5 minutes.
XXIX..	1·0 „	6·0 „
XXX..	1·0 „	5·0 „

Zinc and Cupric Oxide.—Similar experiments were made with the ordinary powdered black oxide of copper. The dry couple when properly made is dark grey, and almost black in colour. A puce colour indicates insufficient heating. The microscope shows a great number of minute metallic particles of the colour of metallic copper or brass. The following were the results obtained :—

Expt.	Cupric oxide.	Time for conversion into ethiodide.
XXXI..	0·5 gram..	7 minutes.
XXXII..	1·0 „	8 „
XXXIII..	1·0 „	6 „

These experiments indicate no great difference between the couples made with metallic copper or either of its oxides, but in order to test this matter more fully we made duplicate series of experiments in an investigation we have since commenced. The result of these experiments was in favour of the metallic copper, as will be seen by the following tables of results. The couples were quite comparable, each quantity of 10 grams being taken from a large specimen. 5 c.c. of ethyl iodide were used in each experiment. The first table gives the comparison for three different temperatures :—

Expt.	Temperature.	Copper oxide.		Copper.	
		Time.	Result.	Time.	Result.
XXXIV..	34° C.	20 mins.	Trace	20 mins.	Slightly more than in CuO experiment
XXXV..	54	20 „	More	20 „	More
XXXVI..	74	9·5 „	Complete	9 „	Complete.

The following table gives the result for various times at the same temperature (54° C.).

Expt.	Time.	Copper oxide.	Copper.
XXXVII..	20 mins.	Trace.	Slightly more than in CuO experiment
XXXVIII..	40 „	Slightly more	Slightly more
XXXIX..	60 „	„ „	Just completing
XL..	80 „	„ „	Complete

The general conclusion from all these experiments on couples, in which the zinc or the copper is replaced by some other body, is, that for practical purposes, no combination has yet been found superior to the copper-zinc couple prepared in the way described above.

LXIII.—*On the Determination of Nitric Acid by means of Indigo, with special reference to Water Analysis.*

By Robert Warington.

My earlier experience of the application of indigo to the determination of nitric acid has been already published (*Chem. News*, **35**, 45, 57). During the last two years a good deal of additional experience has been acquired, and the nitric acid in a large number of drainage waters has been determined by means of indigo in the Rothamsted Laboratory. As the use of indigo affords the speediest means of determining the nitrates present in water, and the method is likely to become generally employed for this purpose, it may be of service to describe the conditions which have been found necessary for its successful application.

The literature of the subject is very voluminous, and has been partially considered in the earlier paper just referred to. The results yielded by indigo are so dependent on the conditions of the experiment, that very various conclusions have been arrived at by different chemists and numerous modifications of method suggested. All that can be done here is to notice occasionally the agreement or disagreement of other experimenters with the plans here suggested.

The form of indigo commonly employed is the sulphindigotate of sodium, known in commerce as "indigo carmine;" it will be found, however, far better to employ a solution of pure indigotin. When the commercial sulphindigotate of sodium is oxidised by nitric acid the

resulting solution is of a deep reddish colour, and the presence of a small excess of unoxidised indigo can be with difficulty ascertained. A solution of sublimed indigotin, on the other hand, yields when oxidised a far paler sherry-coloured solution in which a small excess of indigo is readily perceived, and can be accurately estimated by the eye. Indigotin has been employed both by Tiemann and by Fischer.

The strength of the indigo solution suitable for water analysis is about one-fourth that of the normal solution recommended by Sutton. The normal solution of indigo is equivalent to a solution of nitrate of potassium containing 0·14 gram of nitrogen per litre. If the indigo is to be used in large quantities, it is perhaps most convenient to prepare it in the first instance of the normal strength, and to dilute it as required.

Four grams of sublimed indigotin will furnish more than 2 litres of normal indigo solution. The indigotin is digested for some hours with five times its weight of Nordhausen oil of vitriol, then diluted with water, filtered, and brought to the volume of 2 litres. The strength of the indigo is next ascertained with a normal solution of nitrate of potassium by the method presently described. The indigo solution, which will be found too strong, is finally diluted, so that 10 c.c. correspond with the same volume of the normal nitre solution. There is no object in bringing the indigo absolutely to the normal strength; a near approximation will suffice. To preserve the indigo solution it is well to add to it 4 per cent. by volume of pure oil of vitriol; indigo so fortified undergoes no change when kept in the dark. The use of sulphuric acid is recommended by Sutton.

The normal indigo is diluted, as required, to four times its volume for the purpose of water analysis, oil of vitriol being added in such quantity as to maintain the proportion of 4 per cent. The indigo solution is to be used in a burette graduated to tenths of a cubic centimetre. The solution is too dark to be seen through. The height of the liquid may be read from its upper surface, or an Erdmann's float may be employed. The solution being slightly viscid, the burette should not be read till the level of the liquid becomes constant.

A series of standard solutions of pure nitre will be required to determine the value of the indigo in nitric acid, as this is not uniform throughout the scale. A normal solution of nitre is first prepared by dissolving 1·011 gram of pure nitrate of potassium, gently fused over a spirit lamp before weighing, in 1 litre of water. From this normal solution other solutions of $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ the normal strength are prepared, and preserved for use.

In water analysis it is most convenient to work with 20 c.c. of the water; when this is done it is necessary to standardise the indigo with 20 c.c. of the $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ nitre solutions. If 10 c.c. of

water are to be employed the indigo must be also standardised with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions. It is most useful to standardise both for 10 c.c. and 20 c.c. of water, as waters of a greater range of strength can then be analysed without dilution. It is unnecessary to standardise with 10 c.c. of the weaker nitre solutions; if the amount of nitrate in a water is no greater than that in the $\frac{1}{8}$ nitre solution, 20 c.c. of the water may be at once taken for analysis.

A large supply of pure distilled oil of vitriol will be required for extensive water analysis. It should be colourless, quite free from nitrous compounds, and contain as little as possible of sulphurous acid, and must be of nearly full gravity. As any variation in the acid affects the determination, it is best to mix the contents of all the bottles purchased before proceeding to standardise the indigo. The oil of vitriol is measured for use in a tolerably wide burette provided with a glass stop-cock.

A further requisite is a chloride of calcium bath, provided with a thermometer; the bath is conveniently made in a porcelain basin. The temperature to be maintained is 140°. As the temperature keeps rising from the evaporation of the solution, it is necessary to bring it down to the required point by the addition of a little water, or chloride of calcium solution, immediately before each experiment. The chloride of calcium bath is not required when strong solutions of nitrate are analysed by a normal solution of indigo, the reaction in such cases being almost immediate. With weak solutions of indigo and nitrate the reaction may take some time, in extreme cases as much as five minutes, and it becomes essential for accuracy that the temperature should be maintained throughout at the normal point.

The standardising of the indigo solution is performed as follows:— 10 c.c. or 20 c.c. of the standard nitre solution are placed in a wide-mouthed flask of about 150 c.c. capacity, as much indigo solution is measured in as is judged sufficient, and the whole mixed. Oil of vitriol is next run from the burette into a test-tube, in quantity exactly equal to the united volumes of the nitre solution and indigo. The contents of the test-tube are then poured as suddenly as possible into the solution in the flask, the whole rapidly mixed, and the flask at once transferred to the chloride of calcium bath. It is essential for concordant results that the oil of vitriol should be uniformly mixed with the solution as quickly as possible. This is especially necessary in the case of strong solutions of nitrate in which the action begins immediately after the addition of the sulphuric acid; with such solutions it is more difficult to get duplicate experiments to agree than with weaker solutions in which the action does not begin at once, and in which therefore time is afforded for mixing. The operator should not attempt to drain the test-tube; the oil of vitriol adhering to the

tube is a fairly constant quantity, and after the first experiment the tube will deliver the quantity measured into it.

It is well to have the flask covered by a watch-glass while holding it in the chloride of calcium bath. The progress of the reaction should be watched, and as soon as the greater part of the indigo has been oxidised the contents of the flask should be gently rotated for a moment. With very weak solutions of pure nitre no change is observed for some time, and it may be necessary in some cases to keep the flask in the chloride of calcium bath for five minutes. If the colour of the indigo is suddenly discharged it is a sign that the nitric acid is in considerable excess, and that a considerably larger amount of indigo must be taken for the next experiment. If some of the indigo remains unoxidised, a little experience will enable the operator to judge its probable amount, and so decide on the quantity of indigo suitable for the next experiment.

The amount of indigo which corresponds to the solution of nitrate is found by a series of approximating experiments made as just described with varying quantities of indigo, the oil of vitriol used being always equal in volume to the united volumes of the nitrate solution and indigo. The determination is finished when a quantity of indigo is left unoxidised not exceeding 0·1 c.c. of the indigo solution used; this amount can be readily estimated by the eye. It is well, until considerable experience has been gained, to check the result by making a further experiment with 0·1 c.c. less indigo, when the colour should be entirely discharged. The tint produced by a small excess of indigo is best seen by filling up the flask with water. The estimated excess of indigo is of course deducted from the reading of the burette.

To reduce the number of experiments required to obtain the result it is well to proceed with some boldness, and ascertain as soon as possible what are the limits between which the quantity of indigo must fall. Seven experiments will be a maximum rarely exceeded; four experiments is about the average required at Rothamsted, where, however, the history of the waters examined is already known.

An attempt has been made to determine the excess of indigo present in the final experiment by means of a solution of permanganate of potassium. This plan, if successful, would greatly shorten the process, as only one experiment made with an excess of indigo would then be required. It was found, however, that the permanganate attacked the oxidised indigo as well as the unoxidised; the quantity of permanganate required to discharge the blue colour was thus greater with strong solutions of nitre, for which much indigo had been employed, than with weak solutions, for which little indigo had been required.

The direction has been given to employ oil of vitriol equal in volume to the united nitrate and indigo solutions. It is most important that

the same proportion of oil of vitriol should be used in every experiment, as the quantity of indigo oxidised is much affected by the proportion of acid present, being considerably greater when the acid equals the volume of the other solutions than when the acid is used in larger proportion. In all the published directions I am acquainted with the oil of vitriol is used in double the proportion here indicated. Not only, however, is the quantity of indigo oxidised much greater with the smaller proportion of acid, but the prejudicial effect of organic matter is less under these conditions, as shown in my earlier paper.

When the indigo solution has been standardised with the series of nitre solutions already mentioned, it will be found that the quantity of indigo consumed is not strictly in proportion to the nitric acid present, but diminishes as the nitrate solution becomes more dilute. In round numbers, a diminution of the amount of nitre present to $\frac{1}{8}$ is accompanied by diminution of the indigo oxidised to $\frac{1}{10}$; or, in other words, if 20 c.c. of the $\frac{1}{8}$ normal solution of nitre require 10 c.c. of indigo, 20 c.c. of the $\frac{1}{64}$ nitre solution will require only 1 c.c. of indigo. This is a very important fact, and necessitates the standardising of the indigo with solutions of graduated strength, so that the value of the indigo may be known for all parts of its scale.

In my earlier paper attention was confined to solutions of indigo of normal strength. It was shown that when using a double volume of oil of vitriol, the quantity of indigo oxidised per unit of nitric acid was distinctly less in weak solutions of nitre than in strong; but when using a single volume of oil of vitriol the proportion of indigo oxidised was nearly constant for considerably varying strengths of nitre solution. Experience has since shown that the last statement does not hold good for weaker solutions of indigo and nitre. With a half-normal solution of indigo, 10 c.c. of a $\frac{1}{4}$ normal solution of nitre will oxidise distinctly less than half the indigo required by 10 c.c. of a $\frac{1}{2}$ normal nitre solution; and with the quarter-normal solution of indigo employed in water analysis, the differences produced by dilution become still more considerable.

In consequence of these facts it becomes necessary to form a table of the value in nitrogen corresponding to each part of the indigo scale, and by the help of this table every analysis subsequently made is calculated. Below is given an ideal table of this description. It is assumed, which is very near the truth, that a diminution to one-eighth in the strength of the nitrate solution is accompanied by a diminution to one-tenth in the indigo consumed. It is further assumed, which is also near the truth, that the alteration in the relation of the indigo to the nitrate proceeds at a uniform rate between the limits actually determined. The following will be the results arrived at when using 20 c.c. of the nitrate solution for each experiment:—

Value of the Indigo in Nitrogen for different strengths of Nitre Solutions.

Strength of nitre solution used.	Indigo required.	Difference between amounts of indigo.	Nitrogen corresponding to 1 c.c. of indigo.	Difference between the nitrogen values.	Difference in the nitrogen values for a difference of 1 c.c. in the amount of indigo.
	c.c.	c.c.	gram.	gram.	gram.
$\frac{1}{64}$ normal ...	10·00	—	·000035000	—	—
$\frac{7}{64}$ " ...	8·71	1·29	·000035161	·000000161	·000000125
$\frac{6}{64}$ " ...	7·43	1·28	·000035330	·000000169	·000000132
$\frac{5}{64}$ " ...	6·14	1·29	·000035627	·000000298	·000000231
$\frac{4}{64}$ " ...	4·86	1·28	·000036008	·000000381	·000000298
$\frac{3}{64}$ " ...	3·57	1·29	·000036764	·000000756	·000000586
$\frac{2}{64}$ " ...	2·29	1·28	·000038209	·000001445	·000001129
$\frac{1}{64}$ " ...	1·00	1·29	·000043750	·000005541	·000004295

The mode of using this table is very simple. Supposing that 20 c.c. of a water have required 5·36 c.c. of indigo, this amount is seen to be 0·5 c.c. above the nearest point (4·86 c.c.) given in the table. We learn from the right-hand column that ·000000149 must consequently be subtracted from the unit value in nitrogen (·000036008 gram) belonging to 4·86 c.c. of indigo. We thus find that the 5·36 c.c. of indigo should be reckoned at ·000035859 gram of nitrogen per cubic centimeter: the water, therefore, contains 9·6 parts of nitrogen as nitric acid per million. If 20 c.c. of the water have required less than 1·0 c.c. of indigo, the unit-value corresponding to 1·0 c.c. of indigo is employed for calculating the result; this will give accurate results if the oil of vitriol employed is quite pure.

It is not necessary in practice to form so complete a table as that now given, it will suffice to determine the indigo with nitre solutions of $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$ normal strength: if another solution is used, that of $\frac{3}{64}$ normal strength seems the most important. It may be sufficient, even, in some cases simply to determine the indigo with the $\frac{1}{8}$ and $\frac{1}{64}$ nitre solutions, and to find all the intermediate values by calculation; examples will be presently given showing the amount of agreement between such calculation and experiment. If 10 c.c. of water are to be employed as well as 20 c.c., separate tables should be formed giving the values of the indigo in each case.

There is one important advantage that follows from this troublesome necessity of standardising the indigo with various nitrate solutions: it tends to remove the errors due to impurities in the oil of vitriol. As the volume of the oil of vitriol used depends far more on the volume of water taken than on the quantity of nitric acid it contains, all

errors due to oxidising or reducing matter contained in the oil of vitriol fall far more heavily on determinations of small quantities of nitric acid than on determinations of larger quantities. Unless, therefore, the oil of vitriol used was absolutely pure, it would always be necessary to standardise the indigo as now recommended, even if the relation of indigo to nitric acid were exactly the same in weak and strong solutions. By standardising as now described, the errors due to the sulphuric acid affect the figures of the table, but not the result of the analysis. Such standardising has also the effect, as far as it goes, of calibrating the burette, any inequalities of capacity falling on the table, and not on the analyses calculated from it.

In standardising the indigo solution, and in the subsequent experiments with it, some regard must be paid to the initial temperature of the solutions. A rise in the initial temperature will be attended by a diminution in the quantity of indigo oxidised; this is most perceptible in the case of the stronger solutions of nitrate. The following table shows the results obtained by standardising the same indigo solution at two temperatures, representing nearly the extreme limits at which the solution would be used in practice. The temperature of the room during the experiment was 10°; for the trials at the higher temperature, the flask containing the indigo and nitrate, and the test-tube containing the oil of vitriol, were placed for some time in a water-bath at 22—23° previously to being mixed.

Indigo Solution Standardised with 10 *c.c. of Nitre Solution.*

Strength of nitre solution.	At 10°.		At 22°.	
	Indigo required (actual).	Indigo calculated from two extremes.	Indigo required (actual).	Indigo calculated from two extremes.
	c.c.	c.c.	c.c.	c.c.
$\frac{1}{4}$ normal...	10·28	10·28	9·76	9·76
$\frac{1}{8}$ „ ...	4·97	4·97	4·78	4·73
$\frac{1}{16}$ „ ...	2·30	2·32	2·18	2·22
$\frac{1}{32}$ „ ...	0·99*	0·99	0·96	0·96

* It must not be supposed that it was possible to work to one-hundredth of a cubic centimeter; in all the figures given the errors shown by calibrating the measuring vessels employed have been taken account of, and minute fractions thus introduced.

Standardised with 20 c.c. of Nitre Solution.

$\frac{1}{8}$ normal ...	10·26	10·26	9·74	9·74
$\frac{1}{16}$ " ...	4·84	4·96	4·65	4·74
$\frac{1}{32}$ " ...	2·21	2·31	2·21	2·24
$\frac{1}{64}$ " ...	0·99	0·99	0·99	0·99

It is seen that a rise of 12° in temperature diminishes the indigo consumed by about 5 per cent. in the case of the stronger solutions of nitrate; it is evident, therefore, that the indigo solution should be standardised at nearly the same temperature at which it is to be used.

In the table the quantity of indigo corresponding to the intermediate strengths of nitre solution has been calculated from the determinations made with the two extreme strengths, to show the amount of accuracy to be attained by this plan; the agreement of calculation with the results actually obtained is sometimes very close, but in others the difference is somewhat greater than the errors of experiment.

If the indigo solution has been standardised with 20 c.c. of the nitre solutions recommended, the operator will be able to analyse waters containing nitric acid up to 17·5 parts of nitrogen per million. If the indigo has also been standardised with 10 c.c. of the $\frac{1}{4}$ and $\frac{1}{8}$ nitre solutions, the operator can, by employing 10 c.c. of the water, extend his range of analysis to waters containing 34 parts of nitrogen per million. Waters stronger than this should be diluted for analysis. The natural error of the determination, shown by the performance of duplicate experiments, will not exceed 1 per cent. of the nitric acid present in the case of waters containing 17 of nitrogen per million, but may amount to 5 per cent. with waters containing as little as 2 of nitrogen per million.

Chlorides are of course generally present in waters containing nitrates, they are not altogether without effect on the determination with indigo. In my earlier paper it was stated that chlorides somewhat diminish the amount of indigo required. This is true in the case of moderately strong solutions, but with weak solutions a contrary effect is observed. The following results were obtained with 20 c.c. of nitre solution, with and without the addition of chloride of sodium:—

Strength of nitre solution.	Initial temperature.	Chlorine per million.	Indigo required.	Increase or diminution of indigo by chlorine.
			c.c.	c.c.
$\frac{1}{8}$ normal.....	10°	None	10·15	—
$\frac{1}{8}$ „	„	100	10·00	−0·15
$\frac{1}{8}$ „	22°	None	9·65	—
$\frac{1}{8}$ „	„	100	9·53	−0·12
$\frac{1}{8}$ „	10°	None	10·25	—
$\frac{1}{8}$ „	„	50	10·10	−0·15
$\frac{1}{32}$ „	„	None	2·25	—
$\frac{1}{32}$ „	„	100	2·35	+0·10
$\frac{1}{32}$ „	„	50	2·35	+0·10

The presence of an abundance of chlorides thus occasioned an error of deficiency of about 1·5 per cent. in the case of a $\frac{1}{8}$ normal solution of nitre, and an error of excess of 4·4 per cent. in the case of a solution of one-quarter this strength. At some point between the two the error was probably nil. The different direction of the error is apparently due to the effect of chlorides on the duration of the reaction. As nitre solutions become weaker the time occupied by the reaction with indigo is lengthened, and the proportion of indigo consumed diminished. In the presence of chlorides the duration of the reaction in weak solutions is much shortened, and the quantity of indigo consumed is consequently increased. In the preceding experiments the time of the reaction in the weak solution was reduced by chlorides from $2\frac{1}{2}$ minutes to half a minute, while with the stronger solution the period (about half a minute) was but little affected.

The error introduced by chlorides is for many purposes insignificant. Thus the two nitre solutions employed above contained 17·8 and 4·3 of nitrogen per million; analysed in the presence of excess of chloride they yielded 17·5 and 4·5 per million. As in water analysis the amount of chlorine is always determined, it would be well to make this part of the analysis preliminary to the nitric acid determination. The indigo might also be standardised with nitre solutions containing excess of chloride, and a small quantity of pure chloride added to all waters deficient in this constituent. Finkener has already recommended the addition of chlorides to the standard nitre solutions.

Nitrites are unfortunately not capable of being determined by indigo; the amount of indigo oxidised is much less than in the case of nitrates, and the reaction is far from being sharp. When a dilute solution of a nitrite is mixed with an appropriate quantity of indigo solution, and oil of vitriol added, an immediate reaction takes place; whereas with a corresponding solution of a nitrate an appreciable time is occupied before the indigo is decolorised. When we next endea-

vour to find the quantity of indigo equivalent to the nitrite, it is found that several different quantities of indigo yield almost the same final tint, and this tint is not discharged by heating in the chloride of calcium bath.

Nitrites may be easily converted into nitrates by treatment with permanganate of potassium, and may then be determined by indigo. A solution of commercial nitrite of potassium, which contained by the Crum-Frankland method 31·5 parts of nitrogen per million, gave only 22·1 parts of nitrogen when tested by indigo previously standardised with a nitrate. The same quantity of nitrite, in a more concentrated form, was treated with solution of permanganate, acidified with sulphuric acid, and permanganate slowly added till decolorisation no longer occurred. The solution was finally brought to the same volume as in the first experiment and tested with indigo; it now yielded 32·4 parts of nitrogen per million.

If chlorides are present as well as nitrites, free chlorine may be produced during treatment with permanganate, and the determination with indigo consequently come out too high; in this case it may be well to make the liquid slightly ammoniacal after the treatment with permanganate, and raise the temperature for an instant to boiling. This mode of proceeding, according to Boussingault, completely removes free chlorine.

The nitrites in a water may generally be converted into nitrates by simply leaving the water for some days in a half-filled stoppered bottle, in a dark place; this plan will of course be unsuitable in the case of a water containing ammonia, as the ammonia would under these conditions be converted into nitric acid.

The weakest point in the indigo method is its behaviour in the presence of organic matter. Boussingault showed long ago that the presence of sugar, gum, dextrin, and gelatin led to very low results, while oxalic, acetic, citric, and tartaric acids were without effect. He also found that the organic matter of rain-water had a marked influence on the result. In Boussingault's method the concentrated nitrate was boiled for some time with hydrochloric acid and a solution of indigo; it did not therefore certainly follow that organic matter would have as great an effect in the far speedier reaction here adopted. I found, however, as mentioned in my earlier paper, that a small quantity of cane-sugar greatly reduced the quantity of indigo oxidised by a nitrate, the effect of the sugar being greater in dilute solutions, in which the reaction was naturally more prolonged. The use of a large proportion of oil of vitriol also increased the effect of the sugar. I have since found that carbolic acid is an energetic reducing agent, while tartaric acid has been proved by several experiments to be without effect.

The first determinations of nitric acid in the watery extract of soils

made by the indigo method gave results closely agreeing with those obtained by the Crum-Frankland method, and I was led to conclude that the soluble organic matter of soils had little influence. The first soils examined were both of them extremely rich in nitric acid, a small quantity of soil thus sufficed for the analysis, and the proportion of soluble organic matter to nitrate in the extract was consequently low. In subsequent analyses of ordinary samples of soil, the indigo method has always given results below those yielded by the Crum-Frankland method, which itself errs on the side of deficiency. The following are determinations of nitrogen existing as nitric acid in surface soils by the two methods; the results are expressed as per million of soil:—

Crum-Frankland method.	Indigo method.
729·3	730·4
222·4	224·6
8·5	6·6
4·5	3·5
3·1	2·2

There can be no doubt, therefore, that the soluble organic matter of soils has an injurious effect on the determination by indigo.

The indigo method cannot be employed with safety for the analysis of waters distinctly contaminated with organic matter. Unfortunately there appears to be no method of determining small quantities of nitric acid that is free from suspicion under these circumstances.

In the case of ordinary drainage waters the agreement between the indigo method and that of Frankland is very good. The following analyses of drainage waters refer to waters collected from unmanured arable land. The figures represent nitrogen per million:—

Crum-Frankland method.	Indigo method.
22·7	23·0
16·6	16·9
13·3	13·8

A series of comparative analyses, by the same two methods, of nitrified solutions of ammonium chloride, has been already published (p. 448 of this volume); the agreement between the results was generally good.

The general conclusion respecting the indigo method for determining nitric acid will be that it is excellently adapted by its simplicity, rapidity, and delicacy for general use in water analysis, but that accuracy can be secured only by working under the same conditions which

obtained when the indigo solution was standardised. In the presence of organic matter, the indications obtained with indigo must be accepted as probably below the truth.

LXIV.—*Notes on the Purple of the Ancients.*

By Edward Schunck, Ph.D., F.R.S.

The colour which in ancient times was extracted from various kinds of shell-fish occurring in the sea, and applied to the dyeing of linen and woollen fabrics, has at all times excited the interest of the curious, and it has been the made the subject of numerous learned treatises. The works of Aristotle and Pliny contain accounts of the shell-fish employed in their days for dyeing purposes, and of the processes by which the dye was extracted and applied.

Modern authors, as Fabius Columna (*Fabii Columnæ Lyncei Purpura*, Romæ, 1616), and Major (*J. D. Majoris in Fabii Columnæ tractatum de Purpura Annotationes*, Kiliæ, 1675) have repeated what the ancients said on the subject, adding critical remarks and observations on the natural history of the animals employed. The art of dyeing purple with shell-fish having fallen into disuse and been forgotten, the details of the process could no longer be observed in practice, and the conditions under which the formation of the colour from a colourless substance, such as the animal organism yields, takes place, remained unknown.

In the year 1683 Cole, of Bristol, discovered on the coasts of Somersetshire and South Wales a species of shell-fish, which, by appropriate treatment, could be made to dye linen and silk a fine purple. His account was sent to the Royal Society, and afterwards published (*Philosophical Transactions*, 1685). In 1710, Reaumur (*Mem. de l'Acad. Royale des Sciences*, 1711) found the same animal, the *Purpura capillus* of conchologists, on the coast of Poitou, and made numerous experiments on the formation of the purple colour under various conditions. In 1736, Duhamel (*Mem. de l'Acad. Royale des Sciences*, 1736) took up the subject, his experiments being made with an animal found on the coast of Provence, probably a species of Murex. In 1803, Bancroft (*Philosophy of Permanent Colours*, **1**, 120), working with the same mollusk as Cole and Reaumur, obtained results confirming and extending those of his predecessors. The results arrived at by these observers may be summed up as follows:—

1. The colour-producing secretion, which resembles pus in appearance and consistence, is contained in a small whitish cyst or vein, placed

transversely under, but in immediate contact with, the shell, and near the head of the animal.

2. This pus-like matter, either diluted with water or undiluted, on being applied to bits of white linen or calico, and exposed to sunlight, rapidly changes its colour, passing from yellow through light green, deep green, and "watchet-blue" to purplish-red or crimson. While these changes are in progress, a strong odour like that of garlic or assafœtida is given off.

3. To produce this change of colour, the light of the sun is essential. It is effected more rapidly by the direct action of the sun's rays than by that of diffused light, but it does not take place in moonlight, or in artificial light. If the linen or other fabric to which the secretion has been applied is kept in the dark, it remains unchanged, but when exposed to the sun it becomes purple, even after the lapse of years, though a little more slowly than at first. The metamorphosis which the change of colour indicates is not sensibly promoted by heat. It proceeds in a vacuum and in hydrogen or nitrogen gas as speedily as in air, on exposure to light. It seems to be hastened by the addition of certain chemical reagents, though these cannot replace sunlight, which is indispensable for initiating the change.

4. The colour produced is remarkably stable, resisting the action of soap, alkalis, and most acids, being destroyed only by nitric acid and chlorine.

In a paper published in 1835, Bizio (*Journ. de Ch. Med.*, **10**, 99) gave an account of some experiments made with the purpurigenous secretion of *Murex brandaris*, which led to the same general conclusions as those arrived at by previous observers. Bizio also examined the colouring matter itself, but his remarks on this part of the subject are of little importance.

The latest research on this subject is that of A. and G. de Negri, who in a memoir "On Indigotin in Animals, or the Purple of the Ancients" (*Gazzetta chimica italiana*, 1875, p. 437), give a short account of their observations on *Murex brandaris* and *M. trunculus*. The authors state that the purpurogenic secretions of these two species are not identical, and that the products which they afford are different. The secretion of *M. braudaris* is photogenic, that is to say, it is not coloured when protected from the action of light, whilst that of *M. trunculus* becomes violet even in the dark by the sole action of the air. The colouring matter obtained from the latter by exposure to the air consists, according to the authors, of two substances, one of which is blue and crystalline, presenting all the characters of pure indigotin, whilst the other, of which the authors say but little, is red.

All observers who have made experiments on the subject agree in

asserting that the action of light is in most cases indispensable in the formation of colouring matter from the purpurogenic secretions of mollusca. Now if the process of decomposition induced by light in these cases were of a purely physico-chemical nature, it would stand alone, I think, as furnishing the only known instance of the actual formation of an organic colouring matter by the sole action of light. This view would not, it is true, be in accordance with popular opinion, which is also that of naturalists in general, as it is usually held that the colours which we see in the tissues of plants and animals are due to solar influence, the fact that the leaves of plants grown in the dark and etiolated, rapidly turn green on exposure to light, being considered a sufficient proof of the truth of this opinion. It may be doubted, however, whether the formation of colouring matter in such cases is due to the direct action of light on some colourless substance, and is not rather an effect of the general stimulus imparted by light to the vegetable or animal organism. Recent researches have proved that in the case of chlorophyll, the direct action of light leads to the decomposition of the substance, which is constantly being reproduced by the organic processes going on in the vegetable cell (*vide* Sachsse, *Chemie u. Physiologie der Farbstoffe*, u.s.w.). Until we succeed in eliminating and removing from all organic influences substances which when exposed to sunlight shall assume a green or any other colour, it must remain doubtful whether the action of light is a direct or indirect one. To the naturalist the distinction may perhaps not be of much importance, but to the chemist all circumstances relating to the genesis of organic colouring matters are of very great interest.

Being anxious to ascertain whether the change of colour induced by light in the colourless secretion found in the bodies of certain mollusca is due to purely physical and chemical causes, or whether it is the result of some vital or fermentative process, and what is the nature of the colouring matters produced, I made some experiments, the results of which are contained in the following notes.

1. *The Chromogen of* Purpura Capillus.

Purpura Capillus, the mollusk with which Cole, Reaumur, and Bancroft made their experiments, occurs abundantly on our coasts. The specimens which I employed were found on rocks at low water near Hastings, and were worked up immediately after being collected, it being essential that only live animals should be used.

On breaking the shell, the pale yellow vein containing the colour-producing secretion is discovered at the back of the animal, and may easily be cut out for examination. Having taken out several of these veins, and spread the yellow viscid secretion on some linen, I found the colour on exposure to light change from yellow to green and then

to purple, in accordance with the statements of previous observers, the peculiar garlic-like odour frequently referred to as accompanying the process being also noticed. The colour so produced is, at least on linen, not peculiarly brilliant, but it seems to be permanent, as it resists the action of soap-liquor.

In order to observe the change of colour it is not necessary to use linen or any other fabric. Having cut out several veins I pounded them in a mortar with the addition of water to a paste, which was strained through cambric to separate particles of animal tissue, and the greenish-yellow emulsion was put aside in a dark closet. No visible change had taken place by the next day, but on pouring some of the emulsion into a test-tube and exposing it to the direct rays of the sun, it became in a few moments of a fine purple colour on the side exposed to the light, while it remained green on the shady side. The remainder of the emulsion being left in the dark for two days remained perfectly unchanged. Some fresh emulsion having been made, it was divided into two parts, of which one was placed at once in the light of the sun, while the other part was boiled for some time, whereby a kind of coagulation was produced, before being exposed to the sun's rays. Both portions became purple at once, no difference in the intensity or shade of colour being perceptible. Hence it may be inferred that a temperature of 100° has no effect either in promoting or retarding the formation of colouring matter, and that the chromogen does not undergo any change at that temperature. These and similar experiments having led to the conclusion that light is the effective agent in producing the metamorphosis of the chromogen of *Purpura Capillus*, I thought it unnecessary to repeat the experiments of Bancroft, proving that the change occurs in a vacuum and in various neutral gases as well as in air.

The change of colour produced by insolation may be distinctly observed in its successive stages under the microscope. Having placed a small quantity of the secretion extracted from a living animal on a glass slide, and put a thin glass cover over it, the microscope showed that the secretion was not homogeneous. It appeared full of round transparent discs, probably oil-drops, and among these were a number of small opaque bodies, which like infusoria were in a state of constant motion, the transparent discs being moved hither and thither as the infusoria-like bodies came into contact with them. On exposure to light reflected from a clear blue sky on the stage of the microscope, the transparent discs first became coloured, appearing as purple objects on a colourless ground; then the ground itself began to be coloured, until at last the whole appeared a purple film, in which the discs were still visible, but no darker in colour than the rest.

A small quantity of the secretion placed between two glass plates was enclosed in a box. After six weeks only one purple spot was to be seen, but on exposure to the sun's rays the whole became uniformly purple, though the change was effected much more slowly than with the fresh secretion. Bancroft, who made a similar observation with portions of the secretion which had been kept for some time, supposes that the retardation is owing to the drying up of the secretion. Another portion of the secretion kept in the dark between glass plates has, after the lapse of seven months, become greenish, but no trace of purple colour is visible.

The purpurigenous secretion of the animal contains, besides the chromogen, a quantity of albuminous and other substances. The albuminous constituents may be separated by means of alcohol or ether, in which the chromogen is easily soluble. On treating a number of veins extracted from fresh animals, after being reduced to a pulp in a mortar, with absolute alcohol or ether in the dark for several hours, a golden yellow liquid is obtained. The dirty grey mass left undissolved, after being filtered off and washed with fresh alcohol or ether, remains quite unchanged on exposure to light, but the yellow liquid or extract is remarkably susceptible to photo-chemical influence. On pouring some of it into a small beaker or a test-tube, and exposing it to the direct rays of the sun, it acquires in a few seconds a greenish colour, and then a purple powder gradually subsides, after which the liquid appears of a much paler yellow than before. The effect of light in this case is as distinctly pronounced as in that of the haloïd salts of silver. Just as sunlight blackens silver chloride, so does it turn the chromogen purple, that is to say, it produces a purple colouring matter by a process which, since it takes place almost instantly in an alcoholic or ethereal solution, is doubtless purely physico-chemical, not vital or fermentative. The greenish colour seen in the liquid during the first stage of the process is probably due to the rays of light reflected from the purple particles passing through a stratum of yellow liquid before reaching the eye. The purple deposit itself is granular and semi-crystalline, and under the microscope is seen to consist of small rosettes or stars.

Sunlight is, however, not the only agent capable of effecting the decomposition of the chromogen, as the following experiment proves. Some veins were immediately after extraction immersed in hydrochloric acid, when they became at once dark-coloured, just as if they had been exposed to light, but whether the colouring matter formed by the action of acid is identical with that produced by insolation is open to doubt. The veins having been left in the acid till the next day, light being excluded, were filtered off, when there was left on the filter a purple mass, which after washing and drying imparted to

boiling alcohol and to glacial acetic acid a fine purple colour. The colouring matter produced by insolation is almost insoluble in these menstrua.

I have not attempted to isolate the chromogen of *Purpura Capillus*. The ethereal extract of the veins left on spontaneous evaporation in the dark a residue consisting of golden yellow crystalline scales mixed with drops of oil. The crystalline scales after pressure between folds of blotting paper still appeared yellow, but no change of colour took place on exposing them to light.

2. *Properties of the Colouring Matter formed by Insolation from the Chromogen of* Purpura Capillus.

In order to obtain the colouring matter produced by the action of light on the chromogen, I cut out the veins of a number of animals, extracted them in the dark with cold alcohol, and exposed the yellow alcoholic solution after filtration to the sun's rays, when the colouring matter was deposited, as just described. I attempted to shorten the process by treating the whole animals after breaking the shells and opening the veins, with ordinary spirits of wine, but the result was unsatisfactory, no colouring matter being formed on exposing the greenish-yellow extract to sunlight.

After working up the veins of 400 animals of various sizes in the way described, my patience was exhausted, and I therefore contented myself with the quantity of substance, minute as it was, I had obtained. The colouring matter was filtered off from the yellow liquid, well washed with alcohol, and then transferred to a weighed porcelain crucible. After drying it had the appearance of a bright purple film covering the bottom of the crucible, and weighed 7 milligrams. The reactions that could be tried with so trifling a quantity were necessarily few, but the substance was so pure, that I think they may as far as they go be relied on as correct. The properties observed are the following:

It is quite insoluble in water, alcohol, and ether.

It is slightly soluble in boiling benzol, and in boiling glacial acetic acid.

It dissolves entirely and with comparative ease in boiling aniline. The solution is at first green, but as it approaches saturation it becomes purplish-blue; on cooling it again becomes green, depositing at the same time small granular masses of colouring matter, and retains at last only a faint greenish tinge. The solution at its darkest stage while still warm, shows a broad but well-defined absorption-band, beginning near the line C of the spectrum and extending beyond D, but as the solution cools, depositing the substance contained in it, the band becomes gradually narrower until it occupies the space midway

between C and D, and it then disappears. The masses of colouring matter deposited from the solution in aniline are seen under the microscope to consist of star-shaped groups of irregular crystalline needles, which, when very thin, show by transmitted light a purple colour, the masses reminding one by their general form and tint of certain seaweeds.

It dissolves on standing in concentrated sulphuric acid. The solution has a dirty purple colour, and shows a broad ill-defined absorption-band between D and E, the green and blue of the spectrum being much darkened. On heating the solution slightly, or allowing it to stand for some time, the colour changes to a bright bluish-green, and it now no longer shows the same absorption-band, but in its stead another in the red. This change of colour is doubtless connected with a change of composition in the substance itself.

It dissolves, though not very easily, in a boiling alkaline solution of stannous oxide. The solution on exposure to the air becomes covered with a blue pellicle just like an indigo vat.

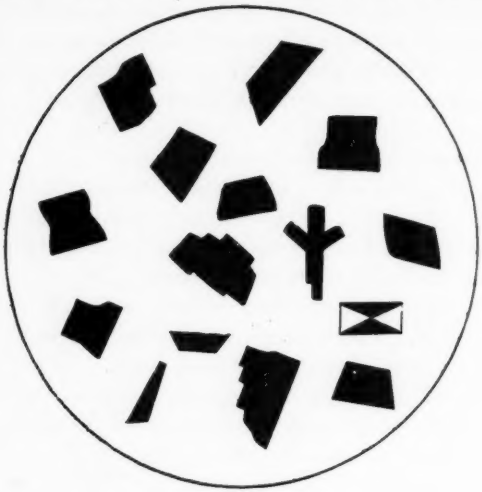
A small quantity of the substance having been put on a watch-glass with a thin glass cover over it, was carefully heated, when it disappeared almost entirely, giving on the cover a sublimate of crystals, which showed by reflected light a semi-metallic lustre like that of sublimed indigo-blue. Examined under the microscope, the crystals were found to have very regular and well-defined shapes, but even the smallest of them were opaque, a few showing at the edges only and in a strong light a deep indigo-blue colour. The slight carbonaceous residue left on the watch-glass on being heated in the open air burnt away, leaving a trace of white ash.

These reactions prove that this colouring matter, though its properties show some resemblance to those of indigo-blue, is not identical with indirubin or any known member of the indigo group, and it being, as I think, a substance *sui generis*, I propose to call it *Punicin*.*

The alcoholic liquid from which the colouring matter had been deposited, left on spontaneous evaporation a yellow residue, of which part was soluble in water. The part left undissolved by water seemed to consist chiefly of fatty matter. The watery solution was yellow, had a strong acid reaction, and contained besides sodium chloride some organic substance which evolved an abundance of ammonia on adding an excess of caustic alkali and boiling. It gave no reaction with Fehling's solution, and therefore contained no glucose.

* "A Phœnicibus, color Phœniceus, puniceus quoque dictus, flagrat velut viola flammea . . . . . Utebantur Veteres quum librorum titulos notarent, colore puniceo, in honorem memoriamque Phœnicum, quos literarum tradunt fuisse inventores."—*Thylesius de Coloribus.*

CRYSTALS OF PUNICIN, SUBLIMED, MAGNIFIED 380 DIAMETERS.



LXV.—*Contributions to the History of Starch and its Transformations.*

By HORACE T. BROWN and JOHN HERON.

EARLY in the present century the attention of chemists was directed to the curious modifications which starch undergoes under the action of heat, acids, and certain vegetable infusions; and owing in part to the great industrial applications of these discoveries, and in part to a belief that a study of the transformations would throw light upon many obscure points in vegetable physiology, the subject has attracted the attention of a great number of observers. Scarcely a year has passed since 1811, unmarked by the production of several memoirs upon starch or its products of transformation. In a catalogue recently prepared by one of us, these original publications are shown to exceed 400 in number. Amongst these there are, it is needless to state, some most valuable memoirs which mark distinct epochs in this special line of research. We may, perhaps, here mention the most important discoveries which lie at the base of all our present knowledge of the subject.

In 1811, Vauquelin (*Bull. Pharm.*, **3**, 54) discovered that starch, on being heated somewhat strongly, is converted into a substance entirely

soluble in water, and possessing many of the physical properties of gum arabic.

Kirchof, in or about the same year (*Schweigg. Journ.*, **4**, 108) found that starch, when boiled with dilute sulphuric acid, yields a crystallisable sugar; and two years later, in 1814, the same chemist observed that a similar transformation is brought about by the action of the vegetable albumin of grain, and that this body has its action much intensified by subjecting the grain to the malting process (*Schweigg. Journ.*, **14**, 389, 1815).

In the year 1812, Vogel (*Schweigg. Journ.*, **5**, 80) found that, in addition to sugar, there is formed a body resembling gum when starch is acted upon by hot dilute acid. This gum was described and examined more fully in 1833, by Biot and Persoz (*Ann. Chim. Phys.* [2], **52**, 72), who gave it the name of *dextrin*, owing to the property it possesses of strongly rotating to the right a ray of plane-polarised light. Biot and Persoz, in this memoir, laid the foundation for the accurate optical methods of the present day, which have yielded such important results in the hands of Bondonneau, Musculus, O'Sullivan, and others. The iodine reaction for starch was discovered as far back as the year 1813, by Stromeyer (*Schweigg. Journ.*, **12**, 349), and the reducing action of the starch-derivatives upon an alkaline copper solution was first investigated by Trommer (*Ann. Chem. Pharm.*, **39**, 360, 1841).

Payen and Persoz, in 1833 (*Ann. Chim. Phys.*, **53**, 73), stated that the action of an infusion of malted grain upon starch is attributable to the presence of a particular transforming agent, which they named *diastase*, from its supposed property of separating the interior of the starch-granules from their outer envelope.

The true structure of the starch-granule was first demonstrated by Fritzche, in an important memoir, published in 1834 (*Pogg. Ann.*, **32**, 129), and this work served some years afterwards as the foundation of C. Naegeli's classical researches on the morphology of the starch-granule, embodied in his celebrated monograph *Die Stärkekörner* (Zurich, 1858).

In the year 1860, Musculus threw an entirely new light upon the action of sulphuric acid and diastase upon starch. It had previously been supposed that the sugar produced in the reaction was a product of the hydration of dextrin, a body intermediate between starch and sugar, and isomeric with the former. Musculus brought forward strong experimental evidence to show that this view of the matter was wrong, and that the sugar and dextrin are produced simultaneously by a splitting up of the starch molecule, accompanied by hydration (*Ann. Chim. Phys.* [3], **60**, 203; *Compt. rend.*, **54**, 194).

Although this theory found strong opponents at the time, and was

attacked by many chemists, notably by Payen and Schwarzer, yet it has stood its ground, and is now pretty generally admitted to be in the main correct.

Since it would be out of place here to attempt even a sketch of the large amount of research based upon the above-mentioned discoveries, we must take up the subject from a point of comparatively recent date.

In a series of remarkable and most important papers, published by O'Sullivan, in the Journal of this Society (*Journ. Chem. Soc.* [2], **10**, 579; *ibid.*, [3], **2**, 125; *ibid.*, [3], **1**, 478), from 1872 to 1876, the author proved that the sugar produced by the action of diastase or acid on starch, is not, as had been almost universally supposed, *dextrose*, but is a sugar of the saccharose type, having a considerably higher optical activity than dextrose, and a much less reducing action upon Fehling's solution.

This body had been previously isolated by De Saussure, in 1819 (*Ann. Chim. Phys.*, **11**, 379), who, however, merely records its crystalline habit, which he describes with accuracy. It was prepared again in 1847, by Dubrunfaut (*Ann. Chim. Phys.* [3], **21**, 178), who recognised it from its optical properties as a distinct sugar, and named it *maltose*. Dubrunfaut's observations, however, obtained but little notice at the time of their publication, and appear to have been entirely forgotten until the re-discovery of maltose by O'Sullivan, many years afterwards.

Having established the principal properties of maltose and dextrin, which, with dextrose, are shown to be the only products obtained from starch, O'Sullivan determined the particular way in which starch is split up under the action of malt-extract, and varying conditions of temperature. His results led him to agree with Musculus, that the transformation of starch into dextrin and maltose is not a gradual act of hydration, the dextrin appearing first, and the maltose afterwards, but that the two bodies are formed simultaneously and in equivalent quantities, by the splitting up of the starch molecule.

The decomposition of starch is considered to take place according to one of the three following equations, the resulting transformation depending upon the temperature employed in the reaction.

$$\text{(A.)}\quad \underset{\text{Starch.}}{C_{18}H_{30}O_{15}} + OH_2 = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}.$$

$$\text{(B.)}\quad \left\{\begin{matrix} C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \end{matrix}\right. + OH_2 = C_{12}H_{22}O_{11} + 4C_6H_{10}O_5.$$

$$\text{(C.)}\quad \left\{\begin{matrix} C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \end{matrix}\right. + OH_2 = C_{12}H_{22}O_{11} + 10C_6H_{10}O_5.$$

The transformation, according to Equation A, is stated to take place when starch-paste is acted upon by malt-extract at any temperature below 63° C.; according to Equation B, at temperatures between 64° and 68—70°; and according to Equation C, at temperatures from 68—70° to the point at which the activity of the transforming agent is destroyed. The specific rotatory power, and the cupric oxide reducing power of the mixed products of transformation corresponding to these equations are:—

	$[\alpha]_j$.	Cupric oxide reducing power per cent.
A	170·6°	44·1
B	191·8	22·4
C	202·8	11·3

The dextrins produced in the above transformations are all considered identical, and capable of yielding maltose by a slow and gradual act of hydration on continuing to digest the solution with malt-extract. By continuing the digestion for many hours, the maltose was found apparently to yield a small quantity of dextrose, or a mixture of dextroses having a united optical activity of $[\alpha]_j + 67°$. This production of dextrose was attributed to the small amount of acid always present in the malt-extract used.

O'Sullivan considers that the results represented by the three equations are due to some change brought about by heat in the character of the transforming agent, and are not due to any difference in the size of the starch molecule.

Märker states (*Landw. Versuchs-Stat.*, **22**, 69: and *Ber. der Naturfor.* München, 1877) that at a temperature of 60° C. four molecules of starch yield three of maltose and one of dextrin; at 65° the yield of maltose is lowered somewhat; and at a still higher temperature two molecules of starch yield one of maltose and one of dextrin.

Märker concludes from this that there are possibly two diastatic ferments, one producing much maltose and little dextrin, and destroyed at a comparatively low temperature; the other producing more dextrin and less maltose, and destroyed at a higher temperature. The latter transforming agent does not act upon dextrin, whilst fresh unheated diastase readily converts it into sugar.

In July of last year Musculus and Gruber (*Bull. Soc. Chim.*, **30**, 54) described the results of a new series of experiments upon starch. They look upon starch as a polysaccharide, containing five or six times the group $C_{12}H_{20}O_{10}$.

Under the action of diastase, or of dilute acids, this carbohydrate undergoes a series of hydrations and successive decompositions, resulting in the production of maltose, and of a new dextrin of less molecular weight. This action goes on by successive stages, until the

γ-achroo-dextrin is reached, which is probably then converted into maltose by a simple act of hydration.

The authors recognise the existence of three distinct achroo-dextrins, (*i.e.*, dextrins which are not coloured by iodine), varying in optical activity and cupric oxide reducing power. These are—

	$[\alpha]_j$.	Cupric oxide reducing power.
Achroo-dextrin α.....	210°	12
Achroo-dextrin β.....	190	12
Achroo-dextrin γ.....	150	28

It will be seen, when we come to describe the results of our own experiments, that we have obtained strong evidence of the non-identity of the achroo-dextrins. We have found them to differ in some of their properties in a way which can be accounted for only by the greater or less complexity of their molecule. These results were obtained some months before the appearance of the above paper of Musculus and Gruber, a fact which we mention, not with any wish to raise the question of priority of discovery, but as affording a greater probability of the correctness of this theory. The optical and other properties of our dextrins do not, however, correspond with those of Musculus and Gruber.

Musculus and Gruber used in their experiments precipitated diastase prepared from malt. We have ourselves made some experiments, using the so-called diastase prepared by Hüfner's glycerin method (*Journ. f. prakt. Chem.* [2], **5**, 372), but have found its action vary very much with its mode of preparation. By repeated solution in glycerin and precipitation with alcohol and ether, the activity of the body is constantly lessened, until a point is reached at which it merely produces limpidity in starch-paste, without any further transformation. During the whole of the following research we have consequently used the cold aqueous infusion of malt as the converting agent, which admits of any degree of accuracy if proper precautions are taken.

Method of Experiment.

All the experiments described in this paper were conducted with potato-starch, which, after being well washed with water, was treated successively with a very dilute solution of potassic hydrate and a 1 per cent. solution of hydrochloric acid. The starch, after being thoroughly washed with water until the last trace of acid had disappeared, was dried at a temperature not exceeding 25° C. Potato-starch thus prepared is, under favourable conditions, so completely transformed by malt-extract as to yield a solution of almost perfect

transparency, the residue from 8 or 10 grams of starch being inappreciable in amount. The ash from a starch treated by this method does not amount to more than 0·15 per cent.

The smaller-grained starches, *i.e.*, those from maize and rice, are purified with greater difficulty by the above treatment, and are consequently less suited for such work as we are about to describe.

In the preparation of the starch-paste the greatest possible care must be taken that the gelatinization is complete, and that the paste is perfectly homogeneous, otherwise it is impossible to obtain uniformity in the results. This end is best attained by mixing the starch thoroughly with a sufficient quantity of cold water to form a thin mud, and then pouring it, with constant and rapid stirring, into water at 100°.

The most suitable quantity of starch to be used per 100 c.c. is from 3 to 5 grams. It is not advisable to have the paste too thick, especially when small quantities of malt-extract are to be used.

The malt-extract was invariably prepared as follows:—100 grams of very finely ground pale malt were mixed with 250 c.c. of distilled water. The mixture, after being well stirred, was allowed to stand from six to twelve hours, and then filtered perfectly bright. The clear filtrate so obtained has a specific gravity of 1036—1040 (water = 1000), varying somewhat with the kind of malt used; this we call *normal malt-extract*, and, except where specified to the contrary, it was with such an extract, after previous treatment in various ways, that all our experiments were conducted.

The specific gravity, optical activity, and cupric oxide reducing power of the malt-extract must be determined, either in the original liquid before treatment of any kind, or after heating and filtration, according to the conditions of the experiment.

A definite quantity of the malt-extract is dropped from a burette, or accurately graduated pipette, into the starch-paste, which has meanwhile been brought in a water-bath to the temperature at which the transformation is to be made. The water-bath is kept at a constant temperature by means of a thermostat. We have found Page's regulator answer the purpose admirably.

At the close of the experiment the volume of liquid, after cooling to 15·5° C., must be measured off, or, if very great accuracy is required, the solution is weighed, and its volume deduced from its specific gravity. If during the transformation it is necessary to take out samples in order to apply the iodine test, these must be carefully measured with a pipette, and allowance made for them in finally determining the total volume of the liquid.

In case the transformation has to be continued for more than 15 to 20 minutes, and the malt-extract employed exceeds 2 or 3 c.c.

per 100 c.c. of starch-paste, it is necessary to digest some of the malt-extract in a separate flask for the same length of time and under the same conditions of temperature as the transformation-liquid itself, the analysis of the malt-extract being made in such a case *after* the digestion. The reason for taking this precaution will be rendered evident when we come to consider the changes brought about in malt-extract by heat.

The solution of the starch-products has now to be analysed. Its specific gravity is first taken at 15·5°, referred to water at 15·5°, and the total solid matter per 100 c.c. is estimated by dividing the specific gravity minus 1000 by the constant 3·86 (water = 1000).*

From the total solid matter thus obtained there are deducted the total solids per 100 c.c. introduced in the malt-extract. The difference gives the number of grams of starch-products per 100 c.c. of liquid.

The cupric oxide reducing power of the liquid must then be determined. This is estimated *gravimetrically* with Fehling's copper solution. Here the precaution of weighing the liquid to be analysed must be taken, for since the quantity required to be used seldom exceeds 5 or 6 c.c., a very small error of measurement would be fatal to accuracy. The volume of the liquid taken is found by dividing the weight in grams by the specific gravity. A sufficient quantity of the liquid is taken to afford from ·2 to ·3 gram of cupric oxide. The reduction with the Fehling's solution is carried on in a water-bath for 12 or 15 minutes. It is not advisable to continue the heating longer if any of the higher dextrins are present, since these are slightly converted by heating with the potash solution. The precipitate of cuprous

* This constant is absolutely correct for solutions of cane-sugar of sp. gr. 1050. We are aware that the true divisor for solutions of dextrin and maltose differs somewhat from this number; but our percentage results will not be influenced by this fact, since the numbers used throughout this paper, representing the specific rotatory powers of maltose, dextrose, and dextrin, and the cupric oxide reducing power of maltose and dextrose, are all calculated for the same constant, 3·86. Although this divisor is fairly correct for solutions of cane-sugar of from 1 to 10 per cent., it is too high for solutions of high specific gravity, the volume occupied by a unit of weight of sugar in a solution of high specific gravity being greater than the volume occupied by a unit of weight in a solution of low specific gravity. In other words, if a given volume of a strong solution of cane-sugar is mixed with a given volume of water, or of a sugar solution of less specific gravity, then the resulting volume will be *less than the sum of the volumes*.

The results of our experiments in this direction with cane-sugar are given in Table I in the form of a curve. By means of this curve we are enabled to ascertain by inspection the divisor to be used for solutions of any specific gravity from 1000 to 1070, in order to determine the number of grams of sugar per 100 c.c. of liquid.

The curve is almost truly parabolic.

oxide, after filtration and drying, is thoroughly oxidised by ignition and then weighed.

The weight of cupric oxide that would be reduced by 100 c.c. of the liquid under examination must then be calculated. If this weight be represented by x, the volume of the liquid taken in c.c. by V, and the weight of the CuO by W, then

$$x = \frac{100\ W}{V}.$$

From the value of x must then be deducted the CuO corresponding with the number of c.c. of malt-extract in 100 c.c. of the transformation-liquid.*

There now only remains to determine the optical activity of the substance.

All the optical determinations were made with a Soleil-Ventzke-Scheibler instrument manufactured by Schmidt and Haensch, of Berlin. The analyser, polariser, and compensator are adjusted so as to give at the zero point a disc of light uniformly illuminated by the so-called "neutral tint," corresponding in refrangibility to the medium yellow ray of the solar spectrum. The solutions of the starch transformation products, which were almost always colourless, were examined almost invariably in a column of 200 mm. in length. In no case was animal charcoal used for decolorising the liquid. The slight difficulty presented by the colour of the malt-extract, in the examination of that liquid, was avoided by using a column 100 mm. in length, and slightly rotating the extra Nicol's prism placed at the anterior end of the instrument for the special purpose of neutralising any slight colour that a solution may possess. The presence of this third Nicol's prism renders the Soleil-Ventzke-Scheibler instrument especially adapted for such observations as we are describing, since in delicate work no reliance can be placed upon decolorisation with animal charcoal: for even when the first portions of the filtrate are rejected, it is seldom that the filtrate from a solution containing much lævorotatory albuminoïds has exactly the same optical activity as the original liquid.

In the instrument used by us we find that 100 divisions of the scale are equal to 38·22 degrees of arc. The error of reading, when a good light and a transparent solution are obtained, does not amount, to

* This method of determining the amount of substance reducing cupric oxide is capable, if all proper precautions are taken, of yielding extremely accurate and concordant results. The severe condemnation of the gravimetrical process recently uttered by Soxhlet (*Chem. Centr.*, 1879, 219) is perfectly unfounded. We state this with great positiveness after upwards of three years' experience of the process, and after carrying out numerous series of test analyses.

a practised eye, to more than one-tenth of a division of the scale, or 2·3 minutes of arc.*

The reading in the 200 mm. tube is divided by 2, and corrected for the deflection due to the malt-extract used.

We have now obtained three factors for the starch transformation-products corrected for the malt-extract used.

(1.) The total solid matter expressed in grams per 100 c.c. (corrected).

(2.) The amount of cupric oxide reduced by 100 c.c. of the solution (corrected).

(3.) The optical activity (corrected) of the solution in the 100 mm. tube expressed in divisions of the Soleil instrument.

From these data we have to deduce the specific rotatory power of the solid substance and its percentage cupric oxide reducing power.

The *absolute* specific rotatory power of a substance is the angular deflection experienced by a ray of plane polarised-light of definite refrangibility on passing through a layer of its aqueous solution 1000 mm. in thickness, and containing 10 grams of the substance per 100 c.c. Where the neutral tint, corresponding with the medium yellow ray of the solar spectrum, is employed, the specific rotatory power is

* We may here notice a curious phenomenon attending the working of the polariscope, to which we believe attention has not been before directed. We find that when the instrument is accurately adjusted to the zero point by one of us (*i.e.*, when the two halves of the disc are illuminated equally by the true neutral tint), the other observer, in order to obtain the same even neutrality, must move the compensator $\frac{2}{10}$ of a division to the right. We imagined at first that this "personal equation" might be due to one of us having a finer appreciation than the other of very small differences of tint; but if this were the case, there ought to be two points equidistant on either side of the true zero point, which would be capable of satisfying the less sensitive eye, for at these two points the colours would be of equal intensity, but reversed in position. As a matter of fact, however, this is not the case, the differences of reading of two observers being *always in the same direction*, and constant in amount. We are at present unable to give a satisfactory explanation of this phenomenon, but believe that it will be found in the region of physiological optics. An examination of the humours of the eye (eye of ox) by one of us has revealed the fact that whilst the aqueous and vitreous humours exert no action whatever on plane-polarised light, the crystalline lens itself has a marked lævorotatory power. We find that a section of the lens, 4·5 mm. thick, is capable of rotating the plane of polarisation for the neutral tint through 1·34° to the left. This lævorotation is as large in amount as is the dextro-rotation of a fourteen per cent. cane-sugar solution in a layer of equal thickness. It is possible that this property of the crystalline lens may have something to do with this question of the "personal equation" of the polariscope: it cannot, however, be the direct and only cause, since the interposition of any substance capable of circular polarisation between the last Nicol and the eye can have no effect in altering the relative tints of the two sides of the illuminated disc.

denoted by the symbol $[\alpha]_j$, whilst $[\alpha]_D$ represents the specific rotatory power for the light emitted by incandescent sodium vapour.*

In such experiments as we are describing, the amount of matter in solution must necessarily be determined from the specific gravity, and since the density of the various carbohydrates in solution differs somewhat, it is evident, when two or more such bodies are present, that the determination of the solid matter will be somewhat complicated. In consideration of this, and also of the still more important fact that, up to the present time, the solution-densities of the carbohydrates have been but very imperfectly determined, we resolved to employ a constant and unvarying divisor for the determination of the solid matter, to which all specific rotatory powers should be referred. This divisor is, as we have before stated, 3·86, and when this number has been used in the determination of the constant, we append it to the ordinary symbol denoting the specific rotatory power, thus $[\alpha]_{j3\cdot86}$. In order to convert $[\alpha]_{j3\cdot86}$ into *absolute* specific rotatory power it is only necessary to increase or diminish the angular value in the proportion of 3·86 to the absolute divisor when this has been determined.

Recent experiments of Tollens and of Schmitz upon dextrose and cane-sugar (*Deut. Chem. Ges. Ber.*, **9**, 1531; *ibid.*, **10**, 1403; *ibid.*, **10**, 1414; *ibid.*, **11**, 1807) indicate that the specific rotatory power of these bodies is not the same in concentrated as in dilute solutions. In the case of cane-sugar, both Tollens and Schmitz found that for highly concentrated solutions the value of $[\alpha]_D$ was sensibly less than for weaker solutions, whilst in the case of dextrose the former observer noticed a marked increase in specific rotatory power in highly concentrated solutions.

It is probable that further research will indicate similar anomalies in the case of all the carbohydrates possessing optical activity, but since the phenomena described are only observed in highly concentrated solutions, they do not affect the accuracy of our experiments, which were all conducted with dilute solutions.

The value of $[\alpha]_{j3\cdot86}$ is thus obtained :—

Let x = the total starch transformation-products in grams per 100 c.c. deduced from the specific gravity, and corrected for the malt-extract.

y = the reading of the solution in the 100 mm. tube expressed in divisions of the scale, and corrected for the malt-extract.

Then

$$[\alpha]_{j3\cdot86} = \frac{3\cdot822\ y}{x}.$$

* The relation of $[\alpha]_j$ to $[\alpha]_D$ for the carbohydrates is 24 to 21·54.

where 3·822 is a constant for the instrument used, 100 scale-divisions being equal to 38·22°.

In determining the cupric oxide reducing power of a substance, O'Sullivan has adopted *dextrose* as his standard of comparison. He defines the cupric oxide reducing power to be "the amount of cupric oxide calculated as dextrose which 100 parts reduce" (*Chem. Soc. J.*, 1876, **2**, 130); hence if the amount of cupric oxide reduced by 1 gram of dextrose is known, the amount of cupric oxide reduced by 1 gram of any substance, calculated upon this number as a percentage, will represent the cupric oxide reducing power of the substance, which we denote by the symbol κ. Here, just as in the case of the specific rotatory power, when the constant 3·86 has been used in determining the value of κ, this number is appended thus: $\kappa_{3\cdot86}$.

The amount of cupric oxide reduced by 1 gram of dextrose has been determined as 2·205 grams. We have satisfied ourselves of the accuracy of this number by repeated experiments with dextrose prepared both by the inversion of cane-sugar and by the action of acid upon starch. The value of $\kappa_{3\cdot86}$ is determined by the formula—

$$\kappa_{3\cdot86} = \frac{100\,y}{2\cdot205\,x}.$$

where

y = grams of cupric oxide reduced by 100 c.c. of the solution after correction for the malt-extract.

x = the total starch-products in grams per 100 c.c. deduced from the specific gravity and corrected for the malt-extract.

Action of Heat upon Malt-extract.

In previous experiments upon starch in which malt-extract has been employed, it has been assumed that the optical activity, cupric oxide reducing power, and percentage of solid matter in the extract are but little liable to change, and that it is necessary merely to determine these factors for a given volume of the cold infusion of malt, or for a definite weight of the malt exhausted with cold water, in order to obtain the correction to be applied to the mixture of the transformation-products. As a matter of fact, however, we find that freshly prepared and filtered malt-extract is constantly undergoing change, even at ordinary temperatures. The result of this change is a gradual increase in specific gravity and cupric oxide reducing power, and a decrease in optical activity. In the cold, and at temperatures below 45° C., the progress of these changes cannot be observed for any length of time, owing to the rapid fermentation to which cold infusions of malt are particularly liable. This fermentation is generally due to

the presence of *Bacillus subtilis*, with the occasional appearance of one or two small species of saccharomyces. If the malt-extract is digested at a temperature of 40—45° C. the saccharomyces do not often appear, the *Bacilli*,* unmixed with any other organism, in 48 hours running through their cycle of growth and development, which terminates in sporulation, and an entire disintegration of the spore-bearing rods. At the same time torrents of carbonic anhydride and hydrogen are evolved in equal proportions, and butyric acid appears in the liquid. If cane-sugar and calcic carbonate, or zinc oxide, are added to a cold water malt-extract, the mixture, submitted to a temperature of 40—45° C., affords an excellent means of obtaining butyric acid, and of studying the organisms active in bringing about the change. Under these conditions little or no lactic acid is formed, or, if formed, is at once converted into butyric acid.

The optical and chemical changes in malt-extract previously referred to are not in any way dependent upon the presence of organised ferments, since the alterations still take place after the malt-extract has been submitted to temperatures sufficiently high to arrest the fermentative activity of such organisms. At 50° C. the changes take place very rapidly and fully. If malt-extract is heated to a temperature higher than 50° for a few minutes, and is, after filtration and analysis, digested for some time at 50°, the above-mentioned changes in specific gravity, optical activity, and cupric oxide reducing power are less rapid and complete the higher the temperature to which the liquid has been heated; showing that heat has a decided weakening action upon the special converting agent. Malt-extract which has been heated above 76° C. undergoes little or no change on subsequent digestion at 50° C. for many hours; a proof that the acids of the malt-extract exert no influence in bringing about the change.

The following examples, taken from a large series of experiments, illustrate what has been said above :—

* Occasionally *Sarcina* will appear.

Experiments illustrating the Action of Heat upon Filtered Normal Malt-extract.

Number.	Description of malt-extract.	Solid matter in grams per 100 c.c.	CuO reduced in grams per 100 c.c.	Deflection in 100 mm. tube, scale-divisions.
1	Malt-extract heated to 58° C. for one hour	9·888	9·261	8·5
2	The same after digestion at 50° C. for 16 hours	10·025	11·798	6·8
3	Malt-extract prepared quickly (one hour).....	9·129	4·857	8·8
4	The same heated for 20 minutes to 60° C.	9·295	6·200	8·8
5	The same heated for 20 minutes to 60° C., filtered, and afterwards digested at 55° C. for 15 hours.....	9·453	9·208	6·7
6	Malt-extract freshly prepared.....	7·759	4·657	7·7
7	The same digested at 58° C. for 15 hours	7·979	7·454	6·3
8	Malt-extract prepared for 16 hours in the cold..	9·956	8·653	8·5
9	The same digested for 16 hours at 55° C.....	10·152	11·263	7·2
10	No. 8 heated to 62° for 20 minutes.....	10·349	9·552	8·8
11	No. 10 digested at 55° for 16 hours	—	11·002	7·5
12	Malt-extract heated to 76° for 20 minutes.....	9·577	6·282	9·4
13	The same digested for 16 hours at 55°	9·549	6·146	9·2
14	Malt-extract quickly prepared and *boiled for 15 minutes*	7·562	5·157	8·0
15	The same digested after boiling at 55° for 16 hours	7·523	5·020	8·3
16	Malt-extract heated to 66° for 20 minutes	9·336	6·185	8·8
17	Digested for 16 hours at 55° after heating to 66°	9·401	7·633	8·5

From the increase in specific gravity observed when malt-extract is digested at a moderate temperature, it is evident that the infusion contains a carbohydrate or carbohydrates capable of hydration.

In the year 1875, Kühnemann announced (*Deut. Chem. Ges. Ber.*, 8, 202; *ibid.*, 387) the discovery of cane-sugar among the soluble constituents of barley malt, and, consequently it seemed to us possible that the changes induced in malt-extract by time and elevated temperature might be due to the inversion of this substance.

If the entire alteration in composition were due to this cause, it is evident that the amounts of cane-sugar, separately calculated from the increased density of the solution, and from the increased cupric oxide reducing power respectively, should correspond within the errors of experiment.

Such, however, is found not to be the case, as will be seen from the following results:—

No. of experiments in previous table.	Cane-sugar in grams per 100 c.c., calculated from hydration.	Cane-sugar in grams per 100 c.c., calculated from increase in CuO reduced.
I and II	2·441	1·155
IV and V	3·038	1·364
XVI and XVII	1·250	0·656

In the above experiments there was no deposition of solid matter on digestion.

The changes in optical activity were too small to afford trustworthy data for calculation, but in all cases the decrease in rotatory power was very much less than would correspond to the inversion of an amount of cane-sugar equal to that given in either of the above series of numbers.

It is evident, therefore, that the above-mentioned modifications in the properties of malt-extract are not at any rate entirely due to the presence of cane-sugar. We have convinced ourselves, however, of the accuracy of Kühnemann's observations. A cold aqueous infusion of malt certainly contains a very appreciable quantity of cane-sugar; and that this cane-sugar must, on digestion, be gradually hydrated s shown by the following experiments, which conclusively prove, we believe for the first time, that malt contains an unorganised ferment capable of inverting cane-sugar :—

Action of Normal Malt-extract upon Cane-sugar.

Series I.—Cane-sugar solution, sp. gr. 1015·26, $[\alpha]_j$ 72·8°; 75 c.c. of sugar solution with 25 c.c. malt-extract.

	$[\alpha]_j$.	Percentage of invert-sugar.
(1.) Cane-sugar solution digested *without* addition of malt-extract at 55° for 16 hours	72·8°	—
(2.) Digested with malt-extract in the cold for 16 hours.....	69·3	3·5
(3.) Digested with malt-extract at 55° for 16 hours	52·6	20·4

Series II.—Cane-sugar solution, sp. gr. 1015·78; 75 c.c. digested with 25 c.c. malt-extract. Action in each case continued *for* 16 *hours*.

(4.) Digested at 45° with malt-extract previously heated for 20 minutes to 60°	66·2°	6·6
(5.) Digested at 45° with malt-extract previously heated for 20 minutes to 66°	71·2	1·6
(6.) Digested at 45° with malt-extract previously *boiled* for 15 minutes.....	72·6	0·2

In No. (2) there was a slight development of bacterial life which may have somewhat influenced the results. The other experiments are free from this objection, not a trace of organic life appearing during the whole time.

It is evident from the results given above, that malt-extract contains an unorganised ferment capable of inverting cane-sugar. This ferment appears to exert its maximum effect at about 55° C., its action being very considerably weakened at 60°, and almost destroyed at 66°. Boiling entirely destroys its invertive power. The organic acids present in malt-extract have no invertive action, the very slight apparent inversion of No. (6) being within the errors of experiment.

We believe that the unstable nature of ordinary cold water malt-extract is mainly attributable to the presence in solution of a small amount of the transformation-products of starch, resulting from the action of the converting agent upon those granules which have been partially disorganised (1) during germination, (2) during the drying of the malt, and (3) during the process of grinding. Under any one of these conditions, as will be shown hereafter, the starch-granules will be attacked by the transforming agent, resulting in the rapid production of maltose, and the lowest achroo-dextrin of the series; the latter body, by the continued action of the malt-extract, being afterwards hydrated. The results obtained on the continued digestion of malt-extract can be readily explained by the simultaneous hydration of a little dextrin and the inversion of cane-sugar.

It is very possible that a cold aqueous infusion of malt may contain other carbohydrates capable of hydration, and derived immediately from the malt, but this is a matter we must leave for further examination. Our object in drawing attention so fully to the changes brought about in malt-extract by heat is mainly to insist upon the great importance, in all experiments on the transformation of starch, of digesting a duplicate sample of the malt-extract under identically the same conditions of temperature, and for the same length of time, as the transformation liquid itself; and of applying to the latter the corrections obtained by an examination of this duplicate sample.

Nature and Properties of Starch and Starch-cellulose.

Starch-granules are built up of distinctly stratified layers, mainly consisting of a substance which has been called by C. Naegeli *granulose*. The outer layers are, as a rule, denser than those nearer the nucleus, and they increase from without inwards in the amount of water which they contain.

Every part of the granule contains, besides granulose, small quantities of another substance, very closely allied to granulose, which has

been called by recent observers *starch-cellulose*. We find that starch-cellulose preponderates in the outer layers of the granule, if indeed the entire outer coating does not consist of this substance. This outer layer is the oldest in point of growth, the starch-granule increasing by intussusception, *i.e.*, the formative material, absorbed from without during the growth of the starch-grains within the protoplasm of the plant cell, is deposited between the already existing particles in the direction of the surface of the layers (C. Naegeli, *Die Stärkekörner*).

To the presence of this protective coating of cellulose is to be attributed the fact that starch-granules when intact are absolutely unacted upon by cold water. Although water is absorbed to a very large extent by the granulose, none of this substance, which is to the highest degree colloïdal, is able to diffuse into the surrounding medium.

When the outer layer of the granule is ruptured by attrition, the contents become much swollen from absorption of water, and a small quantity of matter having all the properties of soluble starch goes into solution. By repeated treatment of the ruptured starch grains with cold water, the greater part of the granulose may be removed, most of the cellulose being left behind in the form of extremely thin layers, which, unlike the granulose, are only coloured by iodine a dirty yellow colour. Granulose itself, and water which has been only for a short time in contact with it, are coloured an intense indigo-blue on the addition of a solution of iodine.

Fr. Schulze (Henneberg's *Journ. Landwirth.*, New Ser., **7**, 214) has obtained starch-cellulose by digesting starch for several days at 60° C. with a saturated solution of common salt containing 1 per cent. of hydrochloric acid.

The same substance was also obtained by C. Naegeli, by acting upon starch at 45—55° C. with saliva, which contains an active agent (ptyalin) capable of attacking and dissolving only the granulose (*Die Stärkekörner*, p. 113).

Finally, Fitz has recently observed (*Deut. Chem. Ges. Ber.*, 1877, 282) that certain schizomycetes can easily ferment the granulose of starch-paste, but leave the starch-cellulose unattacked.

We have found that the action of malt-extract upon starch-paste in the cold affords a ready means of obtaining the cellulose of the starch-granule in large quantities. A starch-paste containing from 5 to 6 grams of starch per 100 c.c. is, when quite cold, treated with about one-tenth of its volume of freshly prepared normal malt-extract. The mixture becomes perfectly limpid in from four to eight minutes, and can then be easily filtered. The flocculent matter left on the filter, after being freed from malt-extract and the products of transformation of the granulose, by washing with cold water, consists of the so-called starch-cellulose. The filtered liquid, at first perfectly bright, becomes

in a few minutes turbid from the separation of a further quantity of flocculent matter which does not appear to differ, except in want of structure, from that previously separated by filtration. This further separation of cellulose is due to the fact that soluble starch and the higher dextrins, the first products of the action of malt-extract upon granulose, are capable of holding some of the cellulose in solution; as the soluble starch and the higher dextrins are degraded most of this separates in the insoluble form. The matter left upon the filter consists of fine laminæ still retaining the shape of the swollen starch-granules, whilst the precipitated portion is of course amorphous.

Starch-cellulose after separation in this way is perfectly insoluble either in cold water or in water at 70—80° C., nor is it possible to dissolve it in solutions of soluble starch or of the higher dextrins. That it is however capable, under certain conditions, of entering into solution is shown by the facts mentioned above, and by the impossibility of preparing it with a very dilute starch-paste, *i.e.*, 1 to 1·5 grams per 100 c.c.*

Insoluble starch-cellulose is not acted upon by malt-extract in the cold, nor yet at a temperature of 60°; we have good reason, however, to believe that the soluble modification is acted upon by malt-extract, somewhat slowly it is true in the cold, but rapidly at temperatures from 50° to 78° C. Proof of these statements will be afforded later on.

Boiling with water converts starch-cellulose to a great extent into soluble starch, the solution having all the optical properties of that body, and yielding the characteristic indigo-blue reaction with iodine. By repeated boiling with water and frequent washing, there is left behind a body upon which a continuation of this treatment has no further effect. This body, amounting to about one-fifth of the original substance acted upon, is readily soluble in a solution of potash, under the action of which it is slowly converted into soluble starch on digestion at an elevated temperature.

It is evident that insoluble starch-cellulose consists of at least two substances, one readily acted upon by boiling water, and the other not. Both these bodies must be very closely allied to granulose, since all these substances yield under favourable conditions soluble starch as the first product of their transformation.

The amount of cellulose which we have obtained from well-washed potato-starch by the above process is from 2·0 to 5·5 per cent., accord-

* C. Naegeli's *granulose* is evidently identical with the *amidone* of Payen and Persoz (*Ann. Chim. Phys.*, **56**, 337, 1834), and with Guérin Varry's *amidine* (*Ann. Chim. Phys.*, **56**, 225); the *amidin tégumentaire* and *amidin soluble* of the latter author being identical with the soluble and insoluble modifications of starch-cellulose.

ing to the previous treatment of the starch during the process of purification. A sample of potato-starch which had been purified by long-continued washing with very dilute potash solution, afforded by the above process 2·46 of cellulose, whilst another sample of the same starch which had been subjected to only a slight treatment with alkali yielded 5·54 per cent.

When starch-cellulose is dissolved in dilute potash solution, the greater part of it can be reprecipitated by the addition of acetic acid, or by passing CO_2 into the liquid. If the alkaline solution is kept at ordinary temperatures and reprecipitated immediately with acid, about 30 per cent. is found to have been converted into soluble starch. If the solution is digested at a moderately elevated temperature, precipitation with acid indicates the formation of a larger quantity of soluble starch. In one case digestion for half an hour at 60° resulted in the recovery of only 57·3 per cent. of the original quantity of cellulose.

The specific rotatory power of an alkaline solution of starch-cellulose appears to be very variable, but always increases on digestion at an elevated temperature. We have found the specific rotatory power of a freshly prepared solution, calculated on the quantity of carbohydrate present, as low as $[\alpha]_j$ 146°, increasing on digestion for a few minutes at 60° C. to $[\alpha]_j$ 173·6°. The rise of angle under these conditions is due to the conversion of cellulose into soluble starch. The entire optical activity of the solution cannot, however, be due to the presence of this latter substance; the cellulose itself must, when held in solution by potash, exert some effect upon polarised light.

When potato-starch is transformed under the influence of malt-extract at temperatures above 45° C., cellulose separates out only when the paste is of a high degree of consistency, and the malt-extract is deficient in quantity; hence it is evident that starch cellulose, at the moment of its separation from granulose, must under these circumstances be readily soluble.

In view of this fact, we have attempted to redissolve starch-cellulose, obtained by the cold process described above, by disseminating it in small quantities through thin starch-paste, and acting upon the mixture with malt-extract at 65°. We have, however, never been successful in obtaining a solution even of a small portion of the cellulose in this way. We believe that there are as well-marked differences between the soluble and the insoluble modifications of starch-cellulose as there are between coagulated and uncoagulated albumin.

Starch-paste.—When starch is treated with hot water the contents of the granules, owing to a large absorption of water, swell up enormously, and ultimately rupturing the outer layer, form a very viscous liquid which is known as starch-paste.

Marked differences in the viscosity of this paste are produced by slight variations in the treatment of the starch during the processes of purification and drying. When it has been treated with potash and acid, a paste of less viscosity will be produced, *cæteris paribus*, than when no such treatment has been adopted. We also find that immense variations in the consistency of the resulting paste are produced by slightly altering the manner of drying the starch. Starch which has been dried slowly and at a low temperature will always yield a more viscid solution than if dried quickly at a more elevated temperature. The following experiments made upon different portions of the same sample of potato-starch will illustrate our meaning.

The relative viscosity of the solutions was measured by the weight required to sink in them a disc of very thin glass, $\frac{5}{8}$ of an inch in diameter.

The paste was made in each case with 3 grams of starch to 100 c.c. of water, but since the samples did not all contain quite the same amount of moisture, the results are corrected for equal weights of dry starch.

No. I. Dried at 50° C. whilst very moist, and afterwards at 100° for 24 hours.

No. II. Dried whilst very moist under the air-pump at ordinary temperatures, and afterwards in the air-bath at 100° for 24 hours.

No. III. Dried under the air-pump and finished at a temperature never exceeding 30° C.

Relative Viscosity of the Paste made with the above Samples. No. I taken as unity.

I	1·000
II	2·306
III	3·288

The differences in viscosity are very remarkable and unexpected. If the statement made recently by Whewell (*Chem. News*, **39**, 97) is correct, that the technical value of a starch varies with its power of producing a more or less viscid paste, we have here a fact of considerable importance to the manufacturer of starch, and one to which, as far as we know, attention has not hitherto been directed.

The following experiments were made in order to determine the specific gravity of starch (*i.e.*, granulose + starch-cellulose) when in the form of paste:—

Experiment I.—2·2500 grams of perfectly anhydrous starch were gelatinised with boiling water, and the volume approximately made up to 100 c.c. at 15·5°. The total weight of the paste was 100·78, and its specific gravity at 15·5° 1008·95, consequently the volume was

99·88 c.c., and 100 c.c. of this liquid would contain 2·2527 grams of dry starch. The specific gravity of starch in the form of paste deduced from these numbers is 1·658 at 15·5°.

Another similar experiment gave 1·662. The mean of these two very closely concordant experiments gives 1·66 as the specific gravity of starch in weak solutions.

From this number can be calculated the divisor which has to be used for starch-paste, in order to convert specific gravities into grams of dry substance per 100 c.c. The general formula is—

$$x = 10\left(1 - \frac{1}{y}\right),$$

where x = the required divisor, y = the specific gravity of the body in solution at 15·5° C. referred to water at the same temperature.

In the case above $x = 3{\cdot}976$.*

There have been from time to time great differences of opinion as to whether granulose exists in starch-paste in a true state of solution, or merely disseminated through the liquid in a finely divided condition. The possibility of separating a great part of the granulose from a moderately thick paste by the ordinary methods of filtration appears at first sight to favour the latter view, which, however, is not necessarily correct, as will be seen from the following considerations. No one doubts that *soluble starch* is capable of forming a perfect solution with water, yet we have found that a solution of this substance on filtration under slight pressure through a thin septum of earthenware, is to a great extent deprived of its solid matter: a porous diaphragm of this kind allowing free passage to the less colloïdal dextrins and all crystalloïds. We believe that these and similar phenomena can be explained in the following way. We have reason to believe that the chemical molecule of an organic colloïdal substance is, as a rule, much more complex than that of any crystalloïd. The same relation probably holds good between the physical "solution-molecules" of the two classes of substances, the solution-molecule being larger the more perfectly colloïdal the substance. When the pores of a filtering medium are small enough to bear a sensible relation to the size of the solution-molecule of the substance, this will be impeded in its passage through the filter, whilst other substances having a less solution-molecule may pass through with facility.

Starch-paste is one of the most perfect colloïds known, and its solution-molecule being very large, its passage through the fine pores of ordinary filter-paper is rendered difficult. The less perfect colloïd,

* If x is known and the value of y is required, the formula becomes $y = \frac{1}{1 - \frac{x}{10}}$.

soluble starch, on the other hand, having a less solution-molecule than granulose, passes readily through ordinary filter-paper, but will not pass through the very fine pores of a septum of earthenware, which is, however, traversed by the less colloïdal dextrins, and with the greatest ease by all crystalloïds.

It appeared to us that the question of granulose existing in starch-paste in suspension or in solution might have some light thrown upon it in a different way.

We know that in most cases of solution the calculated mean of the volumes of the body and its solvent is almost always greater than the observed volume; or in other words, that a substance has a higher specific gravity in solution than when merely in a state of suspension. We have shown that the specific gravity of starch in the form of paste is 1·66. Starch gelatinised with water and precipitated with alcohol, has, after perfect drying, a specific gravity of 1·513. Hence it is extremely probable that granulose exists in starch-paste in a state of true solution.

Optical Activity of Starch-paste.—The determination of the optical activity of starch-paste is a matter of considerable difficulty, owing to the want of transparency in the liquid, and the difficulties attending the filtration of so viscous a solution.

It is not possible to obtain good observations with starch paste containing more than 1 gram of substance per 100 c.c., and even less has to be used if the starch has not undergone a lengthy treatment with dilute potash, in order to remove some of the cellulose.

The following results were obtained with gelatinised starch, the amount of matter in solution in No. I being 1·054 gram per 100 c.c., and in No. II, 1·00 gram.

	$[\alpha]_{j3\cdot86}$	$[\alpha]_j$ absolute.
I	202·1°	208·8°
II	201·1	207·3

On boiling No. II for half an hour, the liquid became much more transparent, and increased decidedly in optical activity.

	$[\alpha]_{j3\cdot86}$.	$[\alpha]_j$ absolute.
II after boiling	213·3°	219·5°

This increase in angle is due to the greater part of the starch-cellulose being converted into soluble starch.

W. Naegeli found the specific rotatory power of a thin boiled starch-paste $[\alpha]$ 198°. Since, however, the solutions upon which this estimation was made contained only ·16 gram of substance per 100 c.c., we cannot but look upon the approximation to correctness as accidental.

Action of KHO on Starch-paste.—When a little of a strong solution

of potash is added to starch-paste, the previously opalescent liquid is rendered perfectly transparent, without any alteration taking place in its viscosity. This increased transparency is brought about by the solution of the suspended integumentary cellulose. The optical activity of the solution is at the same time much reduced by the addition of the first portions of the potash solution, but rises again to its original height, or in some cases a little higher, when the alkali is neutralised by acetic acid or carbonic anhydride. These phenomena are dependent upon the production of a definite compound of starch with potash. Such a body has been described by Schmidt (*Ann. Pharm.*, **51**, 31), and by Ventzke (*Journ. prakt. Chem.*, **25**, 65), but the latter observer has erroneously stated that it has no action on polarised light.

We have obtained the following numbers expressing the specific rotatory power of the starch potash compound. The results are calculated on the quantity of starch present in the combination:—

	Starch with KHO.	After acidification with acetic acid.
	$[\alpha]_{j3\cdot86}$.	$[\alpha]_{j3\cdot86}$.
I	172·3°	198·8°
II	169·4	200·3
III	171·0	—
IV	174·2	206·8

In another experiment in which the potash compound was decomposed with CO_2. the following results were obtained:—

	Starch with KHO.	After decomposing with CO_2.
	$[\alpha]_{j3\cdot86}$.	$[\alpha]_{j3\cdot86}$.
V	166·9°	216·9°

Not a trace of sugar capable of reducing CuO was produced in these experiments, nor was there any considerable production of soluble starch unless the digestion with potash was continued for some time and at an elevated temperature. After acidification the solution remained transparent, and possessed all, or nearly all, the viscosity of the original starch-paste.

When soluble starch is acted upon with potash, the optical activity of the resulting compound is $[\alpha]_{j3\cdot86}$ 182·6°, that of soluble starch itself being $[\alpha]_{j3\cdot86}$ 216·0°.

A body possessing exactly these properties, and perfectly soluble in hot water with complete limpidity, may be separated in small quantities from a boiled starch-paste, by careful fractional precipitation with alcohol. Being somewhat more soluble than granulose, it is found in solution after that substance is no longer soluble in the dilute alcohol. It is no doubt due to the variable quantity of this substance,

soluble starch, and to the variable quantities of starch-cellulose, that is to be attributed the want of closer concordance in the numbers obtained for the optical activities of starch-paste given above. The value of $[\alpha]_j$ for the pure potash compound of granulose is probably 165—168°.

Properties of Maltose.

When estimating the maltose present in a solution of the transformation products of starch by means of the gravimetrical cupric oxide method, we always found that the calculated value of $[\alpha]_j$ for the mixture was higher than the specific rotatory power observed. We were for a time unable satisfactorily to explain this want of coincidence. It was evident from its constancy in direction and amount that it could not be due to errors of experiment, neither did it seem probable that it was owing to the production of a little dextrose, otherwise the difference would have shown a constant tendency to increase, which was not the case. The only explanation possible seemed to be either that numbers too high have been taken for the specific rotatory powers of maltose and dextrin, or that the number 65 given by O'Sullivan as the cupric oxide reducing power of maltose is excessive. The latter seemed by far the more probable explanation, since we noticed that the difference between the observed and calculated numbers increased *pari passu* with the percentage of maltose, being greatest in the most complete transformation, and almost disappearing when the maltose only amounted to 10 or 15 per cent.

In order to investigate this important matter, we prepared maltose on several different occasions, using the method recommended by O'Sullivan, viz., exhaustion with alcohol of the syrupy mass obtained by evaporating a solution of dextrin and maltose prepared from starch. For this purpose as complete a transformation as possible should be made under the conditions mentioned later on.

The maltose on crystallising out was washed with alcohol and recrystallised, until its properties were constant. By a little management this point may be reached on the second crystallisation.

Solution Density.—We find that anhydrous maltose has a somewhat higher specific gravity in solution than cane-sugar at an equal density. A solution containing 5·0655 grams of anhydrous maltose per 100 c.c. has a specific gravity at 15·5° of 1019·915, hence the divisor to be applied to a 5-gram solution in order to calculate the number of grams per 100 c.c. is 3·9314.

Specific Rotatory Power.—The specific rotatory power was found in several different experiments to be as follows:—

Specific Rotatory Power of Maltose.

	$[\alpha]_{j3\cdot86}$.	$[\alpha]_j$ absolute.
(1.)	150·7°	—
(2.)	150·9	—
(3.)	150·1	—
(4.)	150·0	—
Mean	150·4	153·1°

The specific rotatory power according to O'Sullivan is $[\alpha]_{j3\cdot85}$ 150·0°, the experiments he quotes giving as a mean 150·2°, a value almost exactly agreeing with ours.

We have estimated with extreme care the cupric oxide reducing power of several samples of pure maltose, and have invariably obtained a number lower than the usually accepted value 65.

The following are some of our results:—

Cupric Oxide Reducing Power of Maltose.

	$\kappa_{3\cdot86}$.	κ absolute.
(1.)	61·0	—
(2.)	60·69	—
(3.)	60·1	—
(4.)	60·67	—
(5.)	61·11	—
(6.)	61·23	—
Mean	60·8	61·9

It is possible that these numbers may be a very little too low, but certainly not to the extent of more than ·5.

We have adopted 61·0 as the true value of $\kappa_{3\cdot86}$ for maltose, and find when this number is used in our experiments instead of 65·0°, that the calculated and observed results agree with the greatest possible closeness.

Action of Dilute H_2SO_4 on Maltose.—We have investigated with very great care the action of dilute sulphuric acid upon maltose.

The action of dilute acid is stated by O'Sullivan to result in the production of a dextrose, or a mixture of dextroses, having the united optical activity of $[\alpha]_j$ + 67·0° (*Chem. Soc. J.*, 1876, **2**, 139).

Tollens (*Deut. Chem. Ges. Ber.*, **9**, 487) has separated from the end products of the action of dilute acid upon starch a dextrose having all the properties of that obtained by the inversion of cane-sugar. The specific rotatory power was found by Tollens to be $[\alpha]_D$ 53·1° = $[\alpha]_j$ 59·1°.

We have prepared the starch-dextrose ourselves, and find its specific rotatory power in 5 to 10 per cent. solutions $[\alpha]_{j3\cdot86}$ 58·65°.

Our experiments point to this dextrose being the *only* end product of the hydration of maltose.

We have found that the best conditions for a favourable hydration of maltose by means of acid, are obtained by digesting the solution for a considerable time at a temperature not exceeding 80—90° C. By keeping the temperature within this maximum limit there is no risk of breaking up the dextrose into ill-defined bodies, giving more or less colour to the solution.

The first stages of hydration take place with considerable rapidity, the solution increasing in specific gravity as its optical activity diminishes. If further proof were required than that already given by O'Sullivan, of maltose being a sugar of the $C_{12}H_{22}O_{11}$ type, it is afforded by this marked increase in specific gravity, accompanied by a diminution in volume, a certain sign of hydration. In this respect maltose exhibits exactly the same phenomena as cane-sugar when undergoing inversion, the increase in total solid matter per cent. at the close of the two reactions being apparently the same.

The fall in optical activity, which was rapid at first, becomes gradually slower and less marked as the cupric oxide reducing power approaches 100. This value for κ is, however, never reached until the value of $[\alpha]_j$ for the matter in solution has fallen to 58—59°.

The following experiment was made upon a solution of pure maltose containing, when acidified, 4·8510 grams of the sugar per 100 c.c.; 5 c.c. of dilute (one-fifth acid) sulphuric acid being used for the reaction:—

Time of digestion.	Temperature.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
1 hour	70°	147·2°	
3 hours	,,	142·4	—
8 ,,	80	114·7	—
15 ,,	,,	98·9	—
20 ,,	85	83·9	—
26 ,,	,,	73·2	97·4
32 ,,	,,	66·6	—
38 ,,	,,	63·6	—
47 ,,	,,	61·3	99·7
53 ,,	90	58·6	—
59 ,,	,,	58·6	100·2

Although the latter part of the reaction is slow, it does not show any tendency to cease until the final angle of 58·6° and the cupric oxide reducing power of 100 are reached. These are the properties of ordinary dextro-glucose.

Action of Malt-extract upon Maltose.—In order to throw light upon the results obtained by the prolonged action of malt-extract upon the transformation-products of starch, it became necessary to investigate the effect of digesting a solution of maltose for a considerable time with an excess of malt-extract.

During this inquiry the same precautions were taken as in ordinary transformations of starch extending over a considerable time, *i.e.*, all the solutions used were carefully weighed and their volume deduced from the specific gravity, whilst duplicate samples of malt-extract were digested for the same length of time as the maltose solution itself, and the corrections applied as usual.

Experiment I. 75·47 c.c. maltose solution, sp. gr. 1020·94, digested with 24·53 c.c. of unheated normal malt-extract at 55° C.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
Original solution	151·4°	60·1
After 3 hours at 55°	148·9	—
„ 16 hours „	148·0	57·9

Experiment II.—71 c.c. of maltose solution digested with 29 c.c. of normal malt-extract at 63°, the malt-extract having previously been heated to 65° for 20 minutes.

After 20 hours' digestion, $[\alpha]_{j3\cdot86}$ 150·5°, $\kappa_{3\cdot86}$ 60·07.

Experiment III.—75·00 c.c. maltose solution, sp. gr. 1027·00, mixed with 25·00 c.c. normal malt-extract previously heated to 55°.

Digestion at 50° C.

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
Original solution	150·7°	66·67
After 16 hours at 50° ..	150·5	60·7

From the above experiments, it is evident that malt-extract does not contain any active agent capable of hydrating maltose. Even the acid, always present in small amount, is unable to effect any change.

Although maltose is a sugar of the saccharose group, it is a much more stable body than cane-sugar, which we have seen is decidedly inverted by malt-extract at the lower temperatures.

Action of Malt-extract upon Starch.

Action upon Ungelatinised Starch.—O'Sullivan has shown (*Chem. Soc. J.*, 1876, **2**, 133) that malt-extract is incapable of acting upon unaltered starch. We can fully confirm this statement after repeated experiment. Even when the contact of malt-extract and starch-granules has been prolonged to a considerable time, we have never, at ordinary temperatures, obtained any evidence of action.

This fact, at first sight, appears to be at variance with the known

disappearance of starch in seeds during the process of germination, a disappearance which has almost invariably been attributed to the action of diastatic ferments. We therefore considered it necessary to investigate more fully than had been hitherto done the phenomena attending the *metastasis* of starch under these conditions.

Our experiments were conducted upon germinating wheat, barley, and oats. In order to render our results more clear, it will be necessary very briefly to describe the principal parts of the fruit of these cereals.

This consists of a cellular *endosperm* rich in starch and surrounded by a layer of rectangular cells containing the so-called *aleurone grains*, which consist for the most part of proteïds.

Immediately around the layer of aleurone cells is the *testa* or envelope of the true seed, and exterior and closely adherent to this the *pericarp*. This combination of fruit and seed is known as a *caryopsis*, and is, in most species of barley, covered with a thick outer skin consisting of the adherent *paleæ*. The paleæ are not adherent to the caryopsis in the case of ordinary wheat, but separate from the grain in the form of chaff.

The *embryo* is enveloped in a cellular mantle which, on the posterior side nearest the endosperm, forms a thick pellate epidermis known as the *scutellum*.

When wheat commences to germinate, the plumula of the embryo on bursting through its envelope finds itself in immediate contact with the inner surface of the pericarp, which in this case, not being sufficiently strong, is ruptured, the plumula continuing its growth outside the grain.

In barley the pericarp is of sufficient strength (even in the case of the so-called naked barley, where the paleæ, as in wheat, are not adherent) to retain the plumula within it. In consequence of this the growth of the plumula takes place between the testa and pericarp, and in very close proximity to the reserve materials of the endosperm, until it finally issues at the end of the grain the farthest removed from the embryo.

The following are the principal physical modifications observed in the endosperm during the growth of the plumula.

The starch-bearing cells in the immediate neighbourhood of the scutellum of the embryo are deprived to a great extent of their protoplasmic lining, and become more or less disintegrated. This action gradually extends in the direction of the length of the grain, being in all cases most marked in the portions of the endosperm nearest an absorptive surface, *i.e.*, the scutellum or the portions of the testa immediately underlying the growing plumula.

The contents of the aleurone cells are considerably modified as the

growth proceeds, and where a grain has been taken in which the cellular structure of the endosperm is of a delicate nature, as in the case of fine barley grown upon light soil, distinct evidence can be obtained of the disappearance and absorption of the cellulose constituting the walls of the more delicate starch-containing* cells.

It is these changes which mainly constitute the malting process.

The metastasis of the reserve materials other than starch is continued by the growing embryo until these begin to fail or are obtained with great difficulty, and then only are the starch-granules attacked.

We will first consider the case of a barley with an endosperm containing cells, the walls of which are delicate and not much thickened by adhering protoplasm, and where in consequence diffusion can take place with a tolerable amount of ease. In such a case as this little or no action upon the starch is apparent until the plumula has grown considerably beyond the apex of the grain. The first signs of action upon the granule are afforded, as might be expected, by those portions of the endosperm which have been the most thoroughly drained of all other formative material, *i.e.*, those in immediate proximity to the scutellum of the embryo. If the growth of the plumula is allowed to continue, the action upon the starch granules is seen to extend in the same direction as did the first disintegration of the cells of the endosperm, that is immediately subjacent to the plumula and in the direction of its growth.

If the cellular tissue of the barley is strong, and the cell walls have a thick albuminous lining, the metastasis of the reserve materials other than starch is much impeded, and the starch-granules at the base of the endosperm are in consequence disintegrated at a much earlier period than when there is no physical impediment to ready absorption.

In the case of wheat the action upon the starch-granules commences long before the endosperm has been modified to its fullest extent. This is due to two causes, first to the comparative tenacity and strength of the cellular tissue produced by thick cell-walls and the large quantity of protoplasm adherent to them, thus producing great difficulty of diffusion; and secondly to the fact that the plumula, not being retained as in barley between the testa and the pericarp, does not in any way contribute to the absorption of the reserve materials, which have consequently all to be taken up by the comparatively small surface of the scutellum. This results in a draining of the portions of

* The disappearance of cellulose during the germination of certain seeds has been previously observed by Sachs. The greater part of the reserve-material constituting the endosperm of the date consists of cellulose which is absorbed during germination by the growing plant.

the endosperm nearest to the embryo of all readily assimilated material, and through this tract all the other formative material has to pass before reaching an absorptive surface. Hence it follows that the less easily assimilated starch may in such a case as this be attacked when abundance of other formative material may still exist in the endosperm.

In the case of barley, owing to the plumula being closely applied to the testa through the entire length of the corn, it is evident that the longest distance which has to be traversed by a particle of matter before reaching an absorptive surface is the shortest diameter of the grain, whilst in the case of wheat, it is the whole length of the grain.

In general terms we may state that in germinating cereals the point of time at which the starch-granules are attacked is dependent upon the relative ease with which the more readily absorbed reserve materials can be obtained.

The first evidence of any action upon the starch-granules is generally afforded by the appearance* of small pits on the surface of the granule, which by-and-bye is traversed radially by fissures, the granulose being at the same time rapidly dissolved. In a comparatively short time there is nothing left of the original granule but a skeleton of starch-cellulose, which retains for a long time the form of the granule, but this, too, at a much later period of the growth of the young plant, is broken up and disappears.

When the outer coating of the granule has been ruptured there can be little doubt that the rapid action upon the granulose is brought about by the diastatic action of the cell-sap. We have made many attempts to obtain this "pitting" of the granule by treating starch in various ways with the aqueous extract of malt, but have, at ordinary temperatures, invariably failed to obtain any result. We are consequently obliged to look upon this phenomenon as one incapable of separation from the living functions of the vegetable cell. We have seen that there are strong indications of an absorption of cellulose by the embryo during the germination of cereals, and it is possible that there is the commencement of a similar action upon the cellulosic envelope of the starch-granule resulting in its partial disintegration and the exposure of the granulose to the solvent action of the cell protoplasm.

Having now ascertained that the integrity of the outer coating of the starch-granule is the cause of its being able to resist the action of the diastatic ferment, it became necessary to study the action of malt-extract upon *bruised* starch. For this purpose starch was triturated with sharp quartz-sand or powdered glass, with the addition of a little

* The pitting of the starch-granules under the above circumstances was first noticed by C. Naegeli (vide *Die Stärkekörner*).

malt-extract. It was found that starch is very readily acted upon under these conditions.

The optical activity of the resulting transformation products is always very low, and in conjunction with the cupric oxide reducing power, does not always give results compatible with the presence merely of maltose and dextrin.

This cannot be due to the presence of dextrose, since, as a rule, on standing for some time, or on digestion at an elevated temperature, the solutions approach more nearly in optical and chemical properties a mixture of dextrin and maltose.

We attribute the disturbing cause to the presence in solution of a little starch-cellulose, which is gradually transformed into dextrin and maltose in the same way as ordinary starch. We shall see when we come to consider the action of malt-extract upon starch paste in the cold, we have in that case evidence of a similar body entering into solution, and that there is a strong probability of its possessing no optical activity.

The starch was in all cases triturated with sand or powdered glass, and normal malt-extract diluted to $\frac{1}{10}$. The malt-extract was treated in duplicate in a similar way to the transformation liquid.

	Grams of matter per 100 c.c. in solution.	Time.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
Experiment I	1·7303	20 hours	152·0°	40
Maltose		65·5		
Dextrin.....		24·9		
Cellulose		9·6		
		100·0		
Experiment II....	2·8497	6 hours	152·2°	52·7
Maltose		86·3		
Dextrin.....		10·5		
Cellulose		3·2		
		100·0		
The same after 20 hours in the cold.....			152·2°	55·8
Maltose		91·4		
Dextrin.....		7·0		
Cellulose		1·6		
		100·0		
The same heated for 30 minutes to 57°.....			152·4°	59·7

	Maltose	97·8		
	Dextrin	2·6		
		100·4		

	Grams of matter per 100 c.c. in solution.	Time.	$[\alpha]_{j3\cdot8\delta}$.	$\kappa_{3\cdot8\delta}$.
Experiment III ..	3·155	4 hours	155·4°	51·0
	Maltose	83·6		
	Dextrin	13·9		
	Cellulose	2·5		
		100·0		
The same after 20 hours in the cold			152·0°	54·4
	Maltose	89·1		
	Dextrin	8·5		
	Cellulose	2·4		
		100·0		
The same after digestion for 30 minutes at 60°			152·0°	55·3
	Maltose	90·6		
	Dextrin	7·4		
	Cellulose	2·0		
		100·0		
Experiment IV ..	1·308	6 hours	131·0°	43·8
The same after lying 24 hours in the cold ..			130·6	51·4
	Maltose	84·2		
	Dextrin	1·9		
	Cellulose	13·9		
		100·0		

Action of Malt-extract upon Starch-paste in the Cold.

Contrary to what is generally believed, the action of malt-extract upon starch-paste in the cold is very energetic and rapid.

When *normal* malt-extract is added at the rate of from 5 to 10 c.c. to every 100 c.c. of a starch-paste containing from 3 to 4 per cent. of solid matter, complete limpidity ensues in from one to three minutes. The solution is, at this moment, at its maximum point of transparency, and iodine immediately afterwards ceases to give a blue coloration. The brown reaction for erythro-dextrin is, however, somewhat more persistent, seldom disappearing within five or six minutes of the com-

mencement of the experiment. If the solution is now filtered from the undissolved starch-cellulose, the filtrate is found to have a very low optical activity, and a cupric oxide reducing power which is incompatible with the assumption of there being nothing but dextrin and maltose produced from the starch. The filtrate, at first perfectly transparent, again becomes turbid on standing, and the turbidity increases slightly for about half an hour. This precipitate consists of a small quantity of starch-cellulose which has gradually become insoluble as the starch products are more degraded.

The optical activity of the solution is at a minimum two or three minutes after limpidity has taken place, and remains constant for 30 to 45 minutes. At the end of this time, always after the deposition of cellulose has ceased, there is a distinct rise both in specific rotatory power and in reducing power, which attains a maximum in about three hours. The respective values of $[\alpha]_j$ and κ are now consistent with the presence of dextrin and maltose only.

We have no doubt that the abnormally low values for these factors obtained soon after limpidity is produced are due to a small quantity of starch-cellulose remaining in solution, the subsequent gradual rise of angle resulting from the breaking up of this dissolved cellulose.

The following results, which are also graphically represented in Table II, may be taken as typical of a starch-transformation conducted under the above-mentioned conditions.

3·7 grams of starch and 10 c.c. of normal malt-extract per 100 c.c. of liquid.

Time.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	Iodine reaction.
5 minutes	154·6°	—	Slightly brown.
15 ,,	154·6	—	None.
30 ,,	154·6	—	,,
60 ,,	157·5	44·1	,,
3 hours	161·6	49·7	,,

The value of κ at the end of 60 minutes indicates the presence of 72·2 per cent. of maltose; if the remainder were dextrin the angle ought to be 167·3° instead of 157·5° actually observed. At the end of three hours, the calculated angle is 162·2° against 161·6° observed.

The separation of a small quantity of starch-cellulose, after the reaction has continued for five or ten minutes, is never accompanied by any appreciable difference in the optical activity of the liquid, a fact which proves that the cellulose in solution has little or no action on polarised light. This is somewhat remarkable, when we consider the comparatively high optical activity possessed by an alkaline solution of starch-cellulose (see page 613).

The final composition of the starch transformation-products ob-

tained by the above process on several different occasions we give below:—

No.	Time occupied in obtaining a maximum angle.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	Composition.		Calculated optical activity.
I	3 hours	161·6°	49·7	Maltose..	81·4	162·2°
				Dextrin..	18·6	
					100·0	
II	3 hours	161·6	49·7	Maltose..	81·4	162·2
				Dextrin..	18·6	
					100·0	
III	1 hour	161·9	49·0	Maltose..	80·3	163·0
				Dextrin..	19·7	
					100·0	
IV	3½ hours	161·9	—		—	—
V	1 hour	162·9	—		—	—
VI	3½ hours	162·6	—		—	—

The solutions having once obtained the composition indicated above do not sensibly alter for several hours. In about 18 hours a small decrease in optical activity is generally appreciable owing to the dextrin being slightly attacked by the malt-extract.

No. II at the end of 30 hours was found to have the following composition:—

$[\alpha]_{j3\cdot86}$	159·5°	Maltose ..	84·4
$\kappa_{3\cdot36}$	51·5	Dextrin ..	15·6
			100·0

The calculated angle corresponding to this composition is $[\alpha]_{j3\cdot86}$, 160·2°.

All our results obtained by the action of malt-extract upon starch paste in the cold have been so extremely constant, and the resulting mixture of the transformation products has proved so very stable in its composition, that we have no hesitation in asserting that there is produced under these conditions a definite molecular decomposition of starch.

The mean of the above experiments gives the following numbers:—

$[\alpha]_{j3\cdot86}$	162·1°
$\kappa_{3\cdot86}$	49·1

This agrees with the composition—

Maltose	80·4
Dextrin*	19·6
	100·0

The equation—

$$10C_{12}H_{20}O_{10} + 8H_2O = 8C_{12}H_{22}O_{11} + 4C_6H_{10}O_5,$$

Starch. Maltose. Dextrin.

requires for the products of transformation—

Maltose ..	80·9	$[\alpha]_{j3\cdot86}$ ..	162·6°
Dextrin ..	19·1	$\kappa_{3\cdot86}$	49·3
	100·0		

These numbers correspond very closely with those obtained in our experiments.

Evidence will be given later on that this is the decomposition towards which all the transformations tend, and that it is the most stable and well-defined of all the decompositions of starch brought about by malt-extract.

Action of Previously Heated Malt-extract upon Starch-paste in the Cold.—When to starch-paste in the cold is added malt-extract which has been previously heated and again cooled to ordinary temperatures, the converting action is, as might be expected, considerably weakened. Little difference, however, is observed in the time of producing complete limpidity under these varying conditions, but the higher the temperature to which the malt-extract has been heated, the longer can starch and erythro-dextrin be observed in the liquid, and *cæteris paribus*, the higher is the observed optical activity at any given time.

There is a most notable difference in the relative transparency of the solutions in the early stages of transformations made in the cold with heated and unheated malt-extract respectively. When the malt-extract has been previously heated to 66°, owing to the comparative slowness with which the soluble starch and higher dextrins are broken up, a great quantity of starch-cellulose is induced by these bodies to enter into solution. When unheated malt-extract is employed, the soluble starch and the higher dextrins are almost instantaneously converted, and consequently exert but little solvent action upon the cellulose. In consequence of this, in the earlier stages of the reaction, the transparency of the solution treated with previously heated malt-extract surpasses that of transformations conducted with unheated malt-extract; in the former case, however, there is a greater subsequent separation of the cellulose than in the latter.

* Throughout this paper the optical activity of the dextrins has been taken as $[\alpha]_{j3\cdot86}$ 216·0°.

The Action of Malt-extract upon Starch-paste at Elevated Temperatures.

In order to investigate the action of malt-extract upon starch-paste at elevated temperatures, it became necessary to devise some means of instantaneously arresting, in a portion of the liquid, all further transformation at any desired point of the reaction. The plan which naturally suggested itself was to raise the liquid to the boiling point. This, however, in rapid transformations, was found to yield by no means good results, for, no matter how quickly the solution might be heated, some further transformation of the starch products always ensued before the action of the diastatic ferment could be arrested by coagulation.

We then turned our attention to the action of *salicylic acid*, and found that we possessed in this body a most perfect agent for arresting the transformation, and one moreover which did not in the slightest degree influence the analytical results. The plan we adopted was to measure off samples of the transformation liquid at the desired moment into a small flask containing two or three centigrammes of salicylic acid. The sample was shaken with the acid whilst hot, and afterwards cooled and analysed at leisure. The specific gravity of the solution was always taken in another portion to which the acid had not been added, and which was taken out and merely cooled down rapidly; the increase in total solids, due to the small amount of hydration during this process being inappreciable.

The following experiments illustrate the marked effects of small quantities of salicylic acid in arresting the transformation of starch by malt-extract.

100 c.c. of starch-paste containing 5 grams starch used in each experiment, with 5 c.c. of normal malt-extract, and the specified quantity of salicylic acid.

Conversion at 58° C.

Grams of salicylic acid per 100 c.c.	Time of complete limpidity.	Time of disappearance of all soluble starch.	$[\alpha]_{j3\cdot86}$.
None	3 minutes	6 minutes	—
0·001	3 „	6 „	—
0·010	3 „	7 „	—
0·020	3 „	10 „	—
0·030	3 „	12 „	179·0°
0·035	3 „	1½ hours	191·5
0·040	4 „	2 hours	194·6
0·050	No action	No action	—
0·075	No action	No action	—
0·100	No action	No action	—

We see that under the conditions of the above experiments, quantities of salicylic acid up to 10 mgms. influence the reaction but little, whilst above this amount the retarding effect of the acid increases rapidly. 40 mgms. almost destroy the activity of the diastase contained in 5 c.c. of normal malt-extract, whilst 50 mgms. completely arrest all action.

It is a remarkable fact that as long as the transforming agent possesses any diastatic power, the times of production of complete limpidity in the starch-paste are sensibly equal.

Since the quantity of salicylic acid requisite to arrest all action varies somewhat, as might be expected, with the quality of malt used, we have here a means of estimating the relative converting power of malt, quite independently of another method which we shall point out further on.

Having now obtained a method of effectively arresting the action of malt-extract at any desired moment, it is only necessary to obtain a series of observations at short intervals of time in order to illustrate graphically the progress of a reaction by means of a curve, the points in this curve being determined by the length of rectangular co-ordinates. The line of the abscissæ is divided into equal parts corresponding to the duration of the action in minutes of time, whilst numbers corresponding to the angular specific rotatory powers between 216° and 150° are represented on the line of the ordinates.

Modification of the Action of Malt-extract by Heat.—It is evident that the varying results obtained by treating starch with malt-extract at different degrees of temperature may be due to one or both of two perfectly distinct causes.

These are (1) the direct influence of heat upon the splitting up of the starch molecule, and (2) the modifications brought about by heat in the transforming agent. O'Sullivan at the close of his last paper (*Chem. Soc. J.*, 1876, **2**, 143) touches upon this question, and inclines to the belief that the various observed decompositions are due entirely to the latter cause. Our experiments perfectly bear out this view of the case, for we find in every instance that the particular phase of the reaction is determined by the previous treatment of the malt-extract used, provided this treatment has been at the same or a higher temperature than that at which the transformation is made. For instance, when the results are shown graphically, the transformations conducted at 60° and 66°, with malt-extract heated respectively to these temperatures, are expressed by two totally distinct forms of curve, which are represented in Tables IV and V. When, however, the malt-extract has been previously heated for a few minutes at 66°, and the transformations are afterwards conducted with this malt-extract at temperatures of 60° and 66° respectively, both curves are found to be identical,

and correspond to that of the higher temperature, as will be seen by a comparison of Tables V and VI.

We may state the proposition in the following general terms for all temperatures above 50° C.:—

*If two different transformations of equal quantities of starch are brought about at different temperatures by equal quantities of a malt-extract, which has been heated for a few minutes to a point identical with or higher than the more elevated of the two temperatures of transformation, then the conversions will be similar in every respect.**

Action of Malt-extract at 40° C.—The action of malt-extract upon starch at 40° differs in several important points from the transformations in the cold.

In the first place, unless the starch-paste is very thick, and the quantity of extract used very small, no separation of starch-cellulose takes place, neither can this body be detected in solution at any point of the reaction, as it is all converted at an early period. Owing to the conversion of the cellulose, at all stages of the transformation the values of $[\alpha]_j$ and κ are perfectly compatible with the presence of dextrin and maltose only. The fall in optical activity speedily attains its lowest limit, and then remains very constant for a considerable time. The limit of the reaction appears to be exactly the same as that in the cold, viz., $[\alpha]_{j\cdot 86}$ 162·6°, and $\kappa_{3\cdot 86}$ 49·3, corresponding to the composition—

Maltose	80·9
Dextrin	19·1
	100·0

The following transformation may be taken as typical. It is represented graphically in Table III.

5 grams starch, and 10 c.c. of normal malt-extract per 100 c.c. of liquid.

Malt-extract previously heated to 40° for 20 minutes.

Temperature of conversion, 40°.

Time.	$[\alpha]_{j\cdot 86}$.	$\kappa_{3\cdot 86}$.	Iodine reaction.
2½ minutes	164·1°	—	Full brown
15 „	163·3	—	Brown
30 „	163·3	48·8	None

From these last numbers is deduced the following percentage composition of the starch products:—

* The production of complete limpidity in starch paste, *i.e.*, the conversion of granulose into soluble starch, appears to be favoured somewhat by higher temperatures, and this independently of the previous treatment of the malt-extract.

Maltose	80·0
Dextrin	20·0
	100·0

This requires $[\alpha]_{j3\cdot86}$ 163·2° and $\kappa_{3\cdot86}$ 48·8.

Since the cessation of the action in the above experiment might be due to the malt-extract having to some extent lost its power, more malt-extract was now added, at the rate of 10 c.c. per 100, and the solution was digested for a further length of time, with the following result:—

After 60 minutes .... $[\alpha]_{j3\cdot86}$ 161·6° $\kappa_{3\cdot86}$ 49·7

The composition—

Maltose	81·3
Dextrin	18·7
	100·0

requires $[\alpha]_{j3\cdot86}$ 162·3° on $\kappa_{3\cdot86}$ 49·7.

The solution could not be digested for any considerable length of time, owing to the extreme rapidity with which fermentation set in. We see, however, that the further production of maltose at the expense of the dextrin is very slow.

Action of Malt-extract at 50° C.—When malt-extract previously heated to 50° is made to act upon starch-paste at that temperature, the result of the action is almost exactly the same as when malt-extract heated to 40° acts upon starch-paste at 40°.

The following are the results of such an experiment. They are given graphically in Table III:—

5 grams of starch per 100 c.c.

10 c.c. malt-extract (previously heated for 20 minutes to 50°) per 100 c.c.

Temperature of conversion, 50°.

Time.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	Iodine reaction.
2½ minutes	168·1°	—	Full brown
5 „	166·5	—	Brown
15 „	166·5	—	„
30 „	162·7	—	No reaction
60 „	162·3	49·6	„

The percentage composition of the liquid at the end of 60 minutes is represented by—

Maltose	81·3
Dextrin	18·7
	100·0

which requires $[\alpha]_{j3\cdot86}$ 162·3°, and $\kappa_{3\cdot86}$ 49·6.

On digesting the solution with a further quantity of malt-extract there was at first little or no action, but at the end of 16 hours the following numbers were obtained for the corrected starch-products:—

$[\alpha]_{j3\cdot86}$ ..... 147·7°
$\kappa_{3\cdot86}$ ..... 60·8

These numbers correspond closely with the properties of *maltose*. Hence the whole of the dextrin has been hydrated, but without the production of any *dextrose*.

Action of Malt-extract at 60° *C.*—When malt-extract is heated to 60—62°, its action is found to be somewhat weakened when compared with that of an equal quantity of the same extract heated only to 50°.

At 60°, according to generally received ideas, the transformation of starch ought to take place according to O'Sullivan's Equation A; *i.e.*, we ought to obtain indications of a stoppage of the reaction, when the value of $[\alpha]_j$ for the mixed products of transformation has fallen to 170°, and the cupric oxide reducing power has reached 44·1°. This, however, is not the case, as will be seen by referring to Table IV, where two transformations at 60° with malt-extract heated to that temperature, are graphically delineated. It will be seen that when 10 c.c. and upwards of malt-extract are used for a normal conversion of 5 grams of starch per 100 c.c., there is no break in the continuity of the reaction, until the final angle of 162—163° is reached, which takes place within a period of time which is, roughly speaking, inversely proportional to the quantity of malt-extract used. It is true that when comparatively small quantities of malt-extract are used, it is possible, by stopping the reaction between about the fifth and twentieth minute, to obtain any desired angle from about 178 to 164°, with the corresponding cupric oxide reducing power; but there is no criterion by which we can judge of the exact moment when to stop the reaction, nor any indication between the points named of any slackening of the reaction which might correspond to a well defined molecular transformation.

The normal transformation of starch-paste at 60° is similar to that which takes place in the cold and at all intermediate temperatures, and is a close approximation to the reaction represented by the equation—

$$10C_{12}H_{20}O_{10} + 8H_2O = 8C_{12}H_{22}O_{11} + 4C_6H_{10}O_5.$$

The following are a few of the final results obtained by acting upon starch under the above conditions:—

5 grams starch per 100 c.c.

The malt-extract was previously heated to 60° for 20 minutes.

Temperature of transformation, 60°.

No. of c.c. of malt-extract used per 100 c.c.	Duration of the reaction.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.
16·6	5 minutes	162·0°	49·2
20·0	15 „	162·4	49·3
10·0	20 „	162·8	49·0
15·0	20 „	163·8	49·3
10·0	60 „	162·9	49·6
15·0	60 „	162·5	50·5
10·0	15 „	162·3	49·3
10·0	60 „	163·6	48·9
	Mean....	162·8	49·3

The mean values of $[\alpha]_j$ and κ in the above reactions, taken at hazard from a large number of experiments, correspond very closely with those demanded by theory:—

$[\alpha]_{j3\cdot86}$ ..... 162·6°
$K_{3\cdot86}$ ..... 49·3

We now give the details of some experiments which show the progress of the transformation as a function of the time; the action having been in each case arrested as described, with salicylic acid. These results are also represented graphically in Table IV.

Experiment I.—6 grams starch and 5 c.c. of malt-extract (previously heated to 60°) per 100 c.c. of liquid.

Temperature of conversion, 60°.

Time.	$[\alpha]_{j3\cdot86}$.	Iodine reaction.
1 minute	—	Blue
2½ minutes	189·6°	Violet
5 „	178·7	Full brown
15 „	166·3	Very light brown
30 „	164·1	None
60 „	163·4	„

At this point more malt-extract was added at rate of 5 c.c. per 100.

90 minutes 162·2°

More malt-extract added at rate of 5 c.c. per 100.

120 minutes 161·7°

More malt-extract at rate of 4 c.c. per 100.

135 minutes 161·2°

Experiment II.—Per 100 c.c. of liquid.
5 grams starch.
10 c.c. malt-extract, previously heated to 60°.
Temperature of conversion, 60°.

Experiment II.—Per 100 c.c., 5 grams starch. 25 c.c. malt-extract heated to 76°. Conversion at 75°.

Time.	$[\alpha]_{j3\cdot86}$.	$K_{3\cdot86}$.	Iodine reaction.
2½ minutes	205·0°	—	Strong reaction for erythro-dextrin
5 „	204·0	—	„ „ „
10 „	200·3	—	Less erythro-dextrin
20 „	197·9	—	Small quantity of erythro-dextrin
30 „	197·9	—	„ „ „
60 „	195·8	21·0	No reaction
10 c.c. of same malt-extract added per 100 c.c.			
70 minutes	194·4°		„
90 „	191·4		„

These experiments, together with others, are given in a graphical form in Tables VIII and IX. Where the malt-extract was not sufficiently heated there was sometimes a sudden fall of angle on adding further quantities, as shown in No. 18, Table IX.

Under the above conditions limpidity of the starch-paste ensues very quickly, and the blue or violet reaction with iodine, indicative of the presence of starch, always entirely disappears in less than two minutes from the commencement of the experiment; these changes in fact taking place with as great, if not somewhat greater, rapidity than at lower temperatures. The iodine reaction for erythro-dextrin is, however, very persistent. The full brown colour, indicating the maximum production of this body, is obtained when the optical activity of the solution has fallen to 202—203°, the complete disappearance of the reaction only taking place at 194°, or a little lower.

According to O'Sullivan, at temperatures from 68° to the point at which the transforming agent is destroyed, starch under the influence of malt-extract affords a dextrin which is not coloured by iodine, and which corresponds to an angle, for the joint transformation products, of 202·8°. We have made very many attempts, varying the method of experiment in all possible ways, to obtain evidence of the existence of such a dextrin, without success. When an angle of 202° to 203° is obtained the solution always gives with iodine the strongest possible brownish-red action, the maximum coloration occurring between these points. We can therefore only conclude that the dextrin of O'Sullivan's equation C is an erythro-, and not an achroo-dextrin. Erythro-dextrin, or α-dextrin, according to the nomenclature of Bondonneau and O'Sullivan, is consequently one of the ordinary transformation-dextrins proceeding from the degradation of soluble starch, and not merely an isomeric modification of that body, as has been generally assumed. We are strengthened in this belief

by the following considerations. It is evident if erythro-dextrin were only an isomeric modification of soluble starch, that it ought to be possible to obtain it from soluble starch without the simultaneous product of maltose. As a matter of fact, however, in every reaction which we have studied, a change in the iodine reaction from the pure blue of soluble starch, indicating the appearance of a trace of erythro-dextrin, is invariably accompanied by the appearance of cupric oxide reducing power in the liquid which previously was unacted upon by Fehling's solution.

Iodine Reactions.—We may here call attention rather more fully to the changes in the iodine reaction observed during the transformation of starch with malt-extract. These changes are best observed in reactions conducted at 66°.

At the moment of complete limpidity iodine gives a deep indigo-blue reaction, which gradually changes as the transformation proceeds, through violet to a deep reddish-brown. This last reaction, intense at first, gradually dies away, until iodine ceases to give any further coloration.

We have satisfied ourselves that these changes of colour from blue to brownish-red are produced by mixtures of the two bodies, *soluble starch* and *erythro-dextrin*. When these substances are isolated and their solutions mixed in varying proportions, on adding iodine all the differences of tint can be obtained which are observed in a starch transformation.

The iodine compounds of these two bodies do not yield, when examined in the spectroscope, any absorption bands, but cut off opposite ends of the spectrum.

Owing to the greater affinity of soluble starch for iodine a trace of that body can be detected in the presence of an excess of erythro-dextrin by adding only a very small quantity of iodine; the violet or blue reaction under these circumstances appearing before the brown of the erythro-dextrin. On the other hand, the affinity of erythro-dextrin for iodine is less than that of the achroo-dextrins.

During the entire progress of starch transformations at 76° we find no indications of the production of any other body besides dextrin and maltose, the angle calculated from the cupric oxide reducing power always agreeing fairly with the observed specific rotatory power. The coincidence is, however, not quite so close as at the lower temperatures, a fact which we are inclined to attribute to the higher dextrins being slightly degraded by the action of the Fehling's solution, a little too much maltose being consequently obtained.

The following are some examples of transformations at 76° arrested at different points:—

	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	$[\alpha]_{j3\cdot86}$ calculated from κ.
(1.)	204·1°	9·4	205·8°
(2.)	198·7	17·9	196·6
(3.)	195·9	20·5	193·8
(4.)	194·1	22·3	191·8
(5.)	194·6	23·0	191·1
(6.)	195·4	18·7	195·8
(7.)	192·1	23·8	190·2

Influence of Neutralisation upon the Action of Malt-extract.—When malt-extract, after being heated to 66° for a few minutes, is fully neutralised with *barium hydrate* and filtered from the resulting precipitate, its subsequent action upon starch-paste is found to be somewhat weakened, although the nature of the transformation curve does not materially differ in general form from that obtained with unneutralised malt-extract heated to 66°. This will be seen on comparing the Curve No. 19, Table X, with the results given on Table VI, where about an equal quantity of unneutralised extract was employed.

If instead of using barium hydrate the malt-extract after being heated to 66° is rendered very slightly alkaline with *sodium carbonate* and then momentarily heated to 66°, the transforming agent is still capable of rapidly reducing the starch products to a specific rotatory power of 194—196°, but beyond this point it is impossible to push the reaction even by repeated addition of the same malt-extract. Malt-extract treated in this way behaves in fact towards starch exactly in a similar manner to malt-extract heated to 75—76°.

The following experiments illustrate these statements. The results are given graphically in Table X:—

Experiment I.—Per 100 c.c.

Starch 5 grams.

16 c.c. malt-extract heated to 66°, and neutralised with Na_2CO_3.

Temperature of reaction 65°.

Time.	$[\alpha]_{j3\cdot86}$.	Iodine reaction.
$2\frac{1}{2}$ minutes	214·0°	Blue
5 „	201·0	Brown
10 „	200·0	„
20 „	193·9	None
30 „	193·9	„
60 „	193·9	„
8·4 c.c. of same malt-extract added per 100 c.c.		
90 minutes	194·0°	„
8 c.c. of same malt-extract added per 100 c.c.		
120 minutes	194·0°	„

Experiment II.—Per 100 c.c.

5 grams starch.

19·8 c.c. of malt-extract treated as before with Na_2CO_3.

Temperature of reaction 65°.

Time.	$[\alpha]_{j3\cdot86}$.	Iodine reaction.
2½ minutes	205·3°	Full brown
5 ,,	201·0	,,
10 ,,	197·8	Light brown
20 ,,	196·0	,,
30 ,,	195·6	None
60 ,,	194·7	,,
10 c.c. of same malt-extract added per 100 c.c.		
90 minutes	194·2°	,,
8·7 c.c. of same malt-extract added per 100 c.c.		,,
120 minutes	192·3°	

When malt-extract heated to 66° is rendered *very slightly* alkaline with *sodium hydrate* the final angle of the starch products is not reduced below 202°, a point corresponding with the maximum iodine reaction for erythro-dextrin in all transformations with malt-extract heated to 66—76°. Subsequent frequent additions of the same malt-extract do not bring down the angle, as is shown in the following experiment, which is also given graphically in Table XI:—

Per 100 c.c.

5 grams starch.

25 c.c. malt-extract heated to 66°, and rendered *very slightly* alkaline with NaHO.

Time.	$[\alpha]_{j3\cdot86}$.	Iodine reaction.	
2½ minutes	207·8°	Violet.	Much starch
5 ,,	204·8	Full brown.	A little starch
10 ,,	204·0	Full brown.	No starch
20 ,,	202·0	,,	,,
30 ,,	202·0	,,	,,
60 ,,	202·0	,,	,,
9·3 c.c. of same malt-extract added per 100 c.c.			
90 minutes	203·0°	Full brown.	No starch
8·2 c.c. of same malt-extract added per 100 c.c.			
120 minutes	203·0°	Full brown.	No starch

If the malt-extract is rendered more than slightly alkaline with soda its diastatic power is quite destroyed.

In all experiments with neutralised malt-extract the modifications of its action were always attended with a distinct precipitation of albuminoïds.

The Molecular Transformations of Starch.—We believe that the experiments described substantiate the existence of at least four well-defined molecular transformations of starch; by far the best defined and the most stable being the ultimate reaction most easily obtained with malt-extract heated not higher than 60°, and having 162·6° for the specific rotatory power of its products, and 49·3 for the cupric oxide reducing power.

The next fixed point is that of the disappearance of the iodine reaction for erythro-dextrin when starch is transformed with malt-extract heated to 66°. This takes place when the value for $[\alpha]_{j3\cdot86}$ is 188·5°, and for κ 25·0 or thereabouts, and is very constant with varying quantities of malt-extract.

The next strongly marked reaction is that obtained with malt-extract heated to 75°, and also with malt-extract heated to 66°, and rendered alkaline with carbonate of soda; the numbers obtained being $[\alpha]_{j3\cdot86}$ 195—196°, and $\kappa_{3\cdot86}$ 18·9.

The highest stable transformation established by our experiments is obtained by the action of malt-extract heated to 66°, and made very slightly alkaline with soda, the same reaction being also marked in all transformations above 66° by the appearance of the maximum iodine coloration for erythro-dextrin. The numbers for this transformation, $[\alpha]_{j3\cdot86}$ 202—203° and κ 12·7, are very nearly those of O'Sullivan's equation C, the dextrin being, however, an erythro-dextrin.

Transformation of the Higher into the Lower Equations.—When the products of a transformation of starch, having an optical activity higher than 162·5°, are treated with a little unheated malt-extract at 50—60°, the specific rotatory power of the matter in solution falls very rapidly to 162·5°, the cupric oxide reducing power at the same time increasing to about 49·3, at which points these factors remain for a time constant. This change, under favourable conditions, takes place *per saltum*, and not by any slow and gradual act of hydration, as will be seen in the following experiments:—

A conversion of starch with malt-extract previously heated to 65° was made in the usual way, the reaction being stopped by boiling in about ten minutes from the commencement. The starch products gave on analysis, after correction, the following numbers:—

$[\alpha]_{j3\cdot86}$	187·8°
$\kappa_{3\cdot86}$	28·9

corresponding to a percentage composition of

TABLE I.

Curve for cane sugar, showing the divisor to be used for solutions of sp. gr. of 1,000 *to* 1,115 (*water* = 1,000) *in order to obtain the number of grms. of dry sugar per* 100 *c.c. of liquid at* 15·5° *C.*

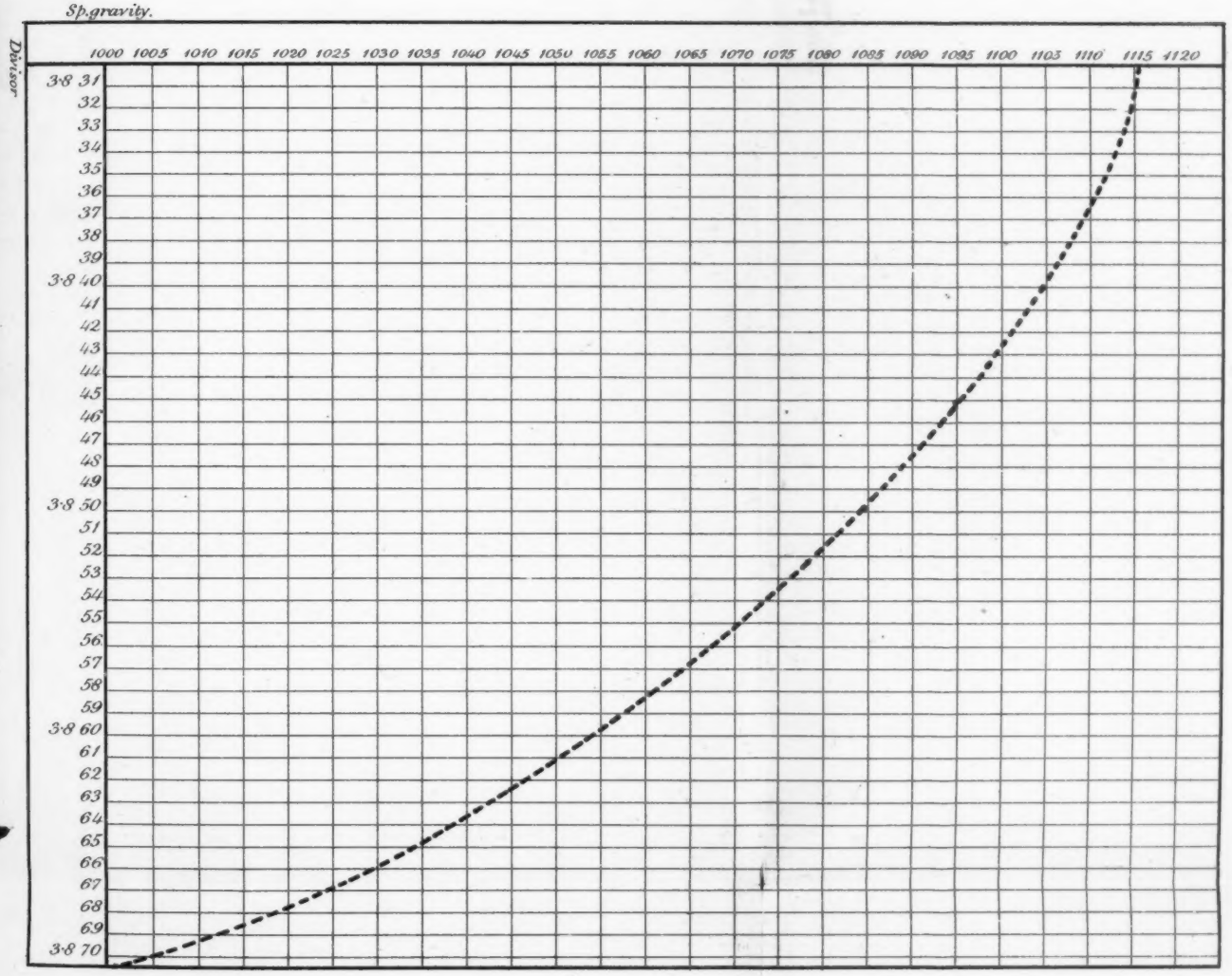


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TABLE II.

Action of (unheated) malt extract on starch paste in the cold.

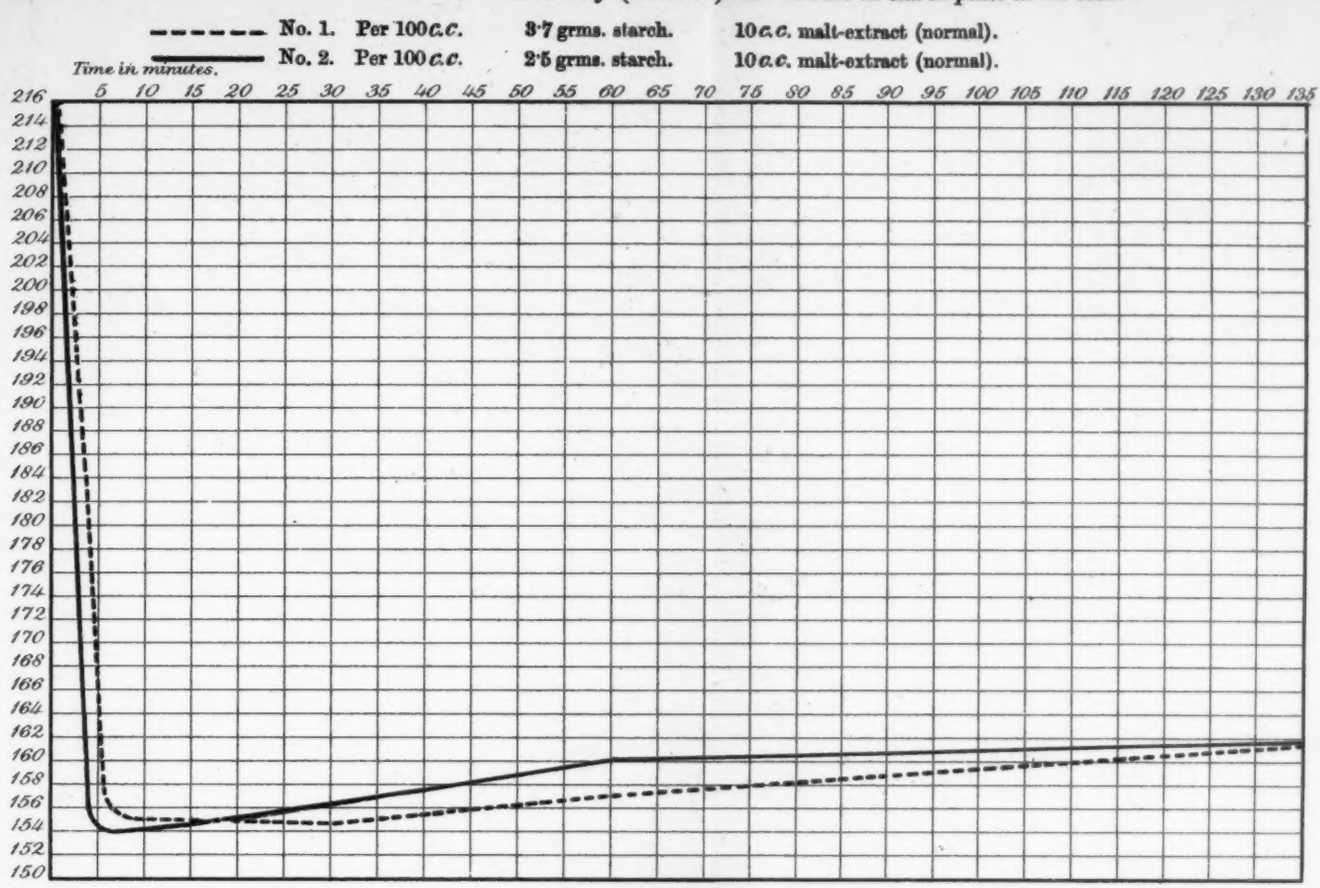

TABLE III.

Transformations at 40° and 50° with malt-extract heated to those temperatures for 20 minutes.

Per 100 c.c. 5 grms. starch. 10 c.c. malt-extract.

No. 3. Transformation at 40°. Malt-extract heated to 40°.
No. 4. Transformation at 50°. Malt-extract heated to 50°.

N.B.—The thick black vertical line indicates the addition of more malt-extract.

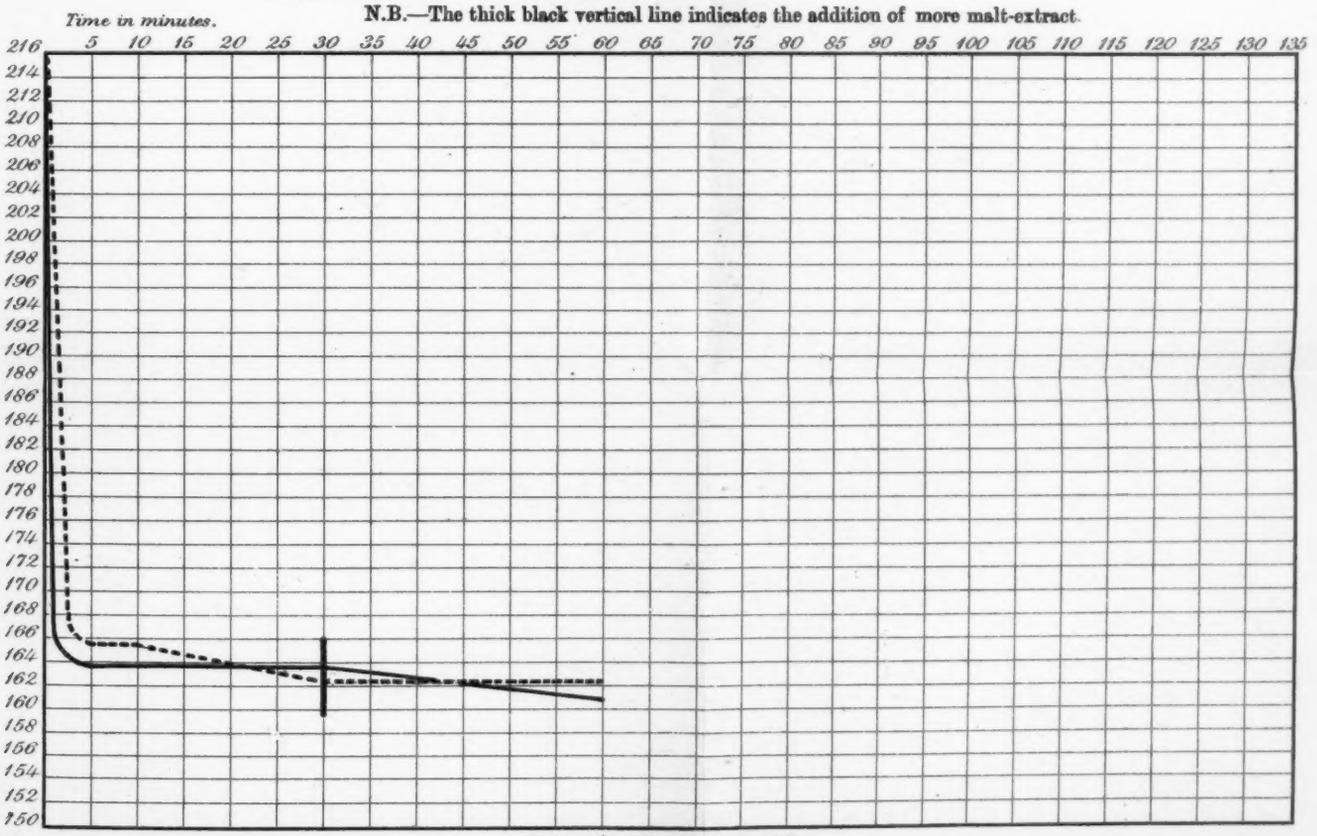

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TABLE IV.

Transformations at 60° with malt-extract previously heated to 60° for 20 minutes.

——— No. 5. Per 100 *c.c.* 5·5 grms. starch. 10 *c.c.* malt-extract.
– – – – – No. 6. Per 100 *c.c.* 5·5 grms. starch. 5 *c.c.* malt-extract.

N.B.—The thick black vertical lines indicate the addition of more malt-extract.

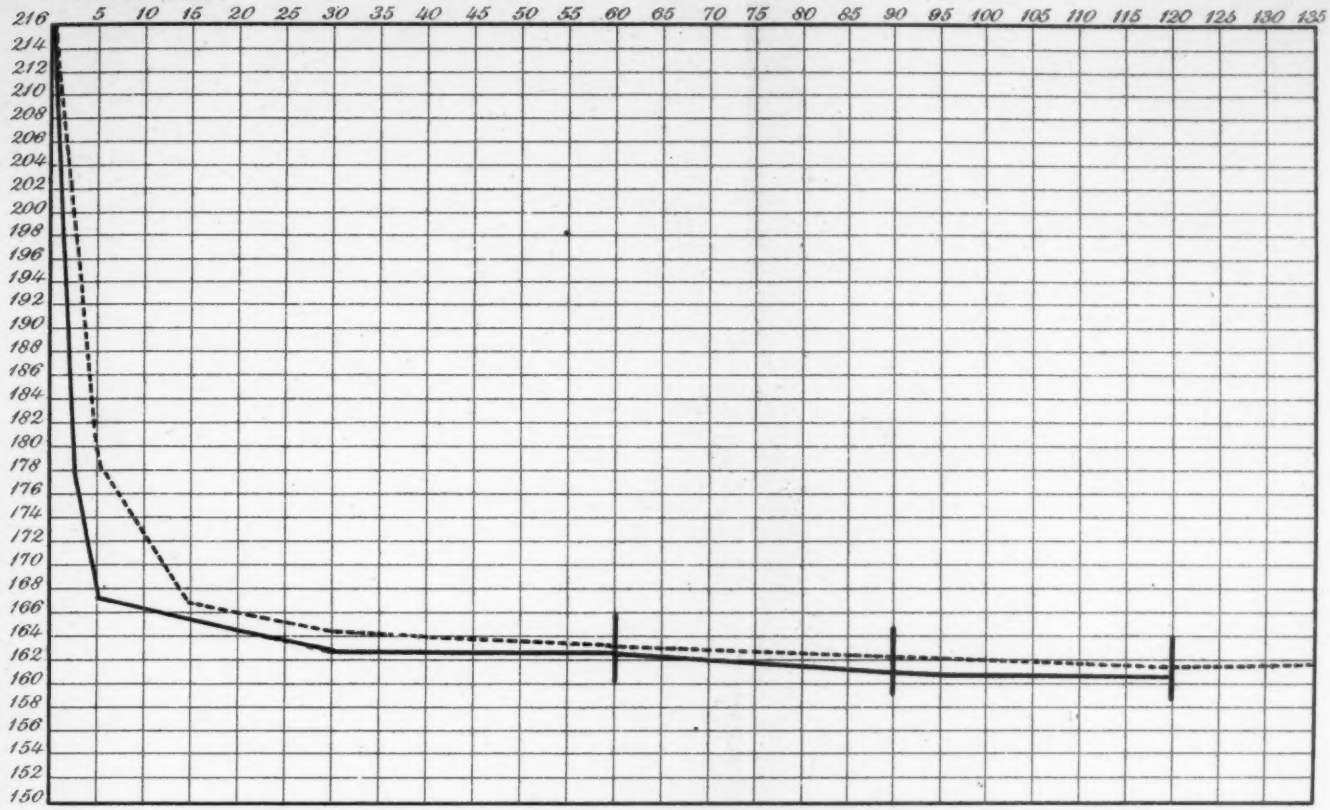

TABLE V.

Transformations at 66° with malt-extract previously heated to 66° for 20 minutes.

Per 100 *c.c.* 6 grms. starch. 8·92 *c.c.* malt-extract.

N.B.—The thick black vertical lines indicate the addition of more malt-extract.

——— No. 7.
– – – – – No. 8.

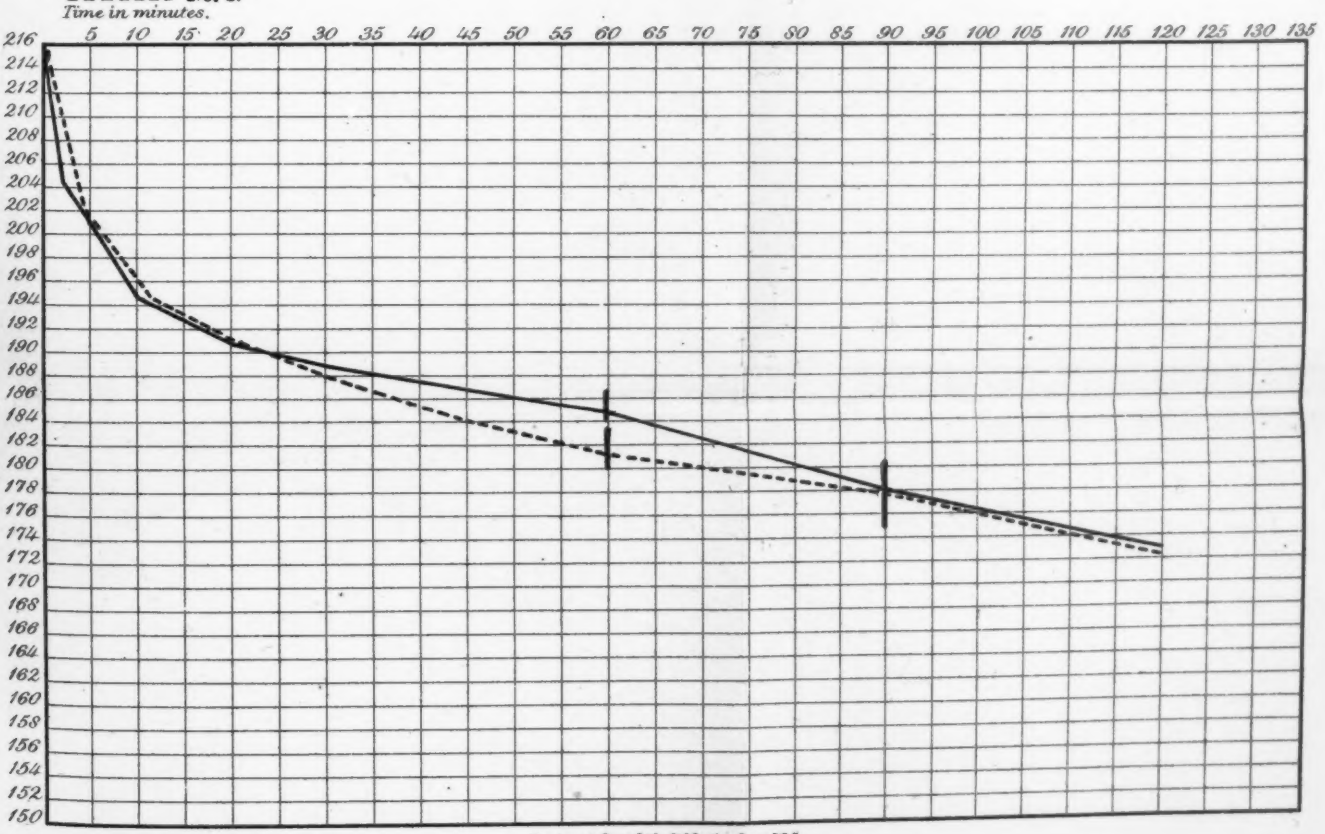

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TABLE VI.

Transformations at 66° and 60°.

No. 9. Malt-extract previously heated to 66° for 20 minutes, conversion at 66°.
No. 10. Malt-extract previously heated to 66° for 20 minutes, conversion at 60°.
Per 100 *c.c.* 5 grms. starch. 15 *c.c.* malt-extract.
N.B.—The thick black vertical lines indicate the addition of more malt-extract.

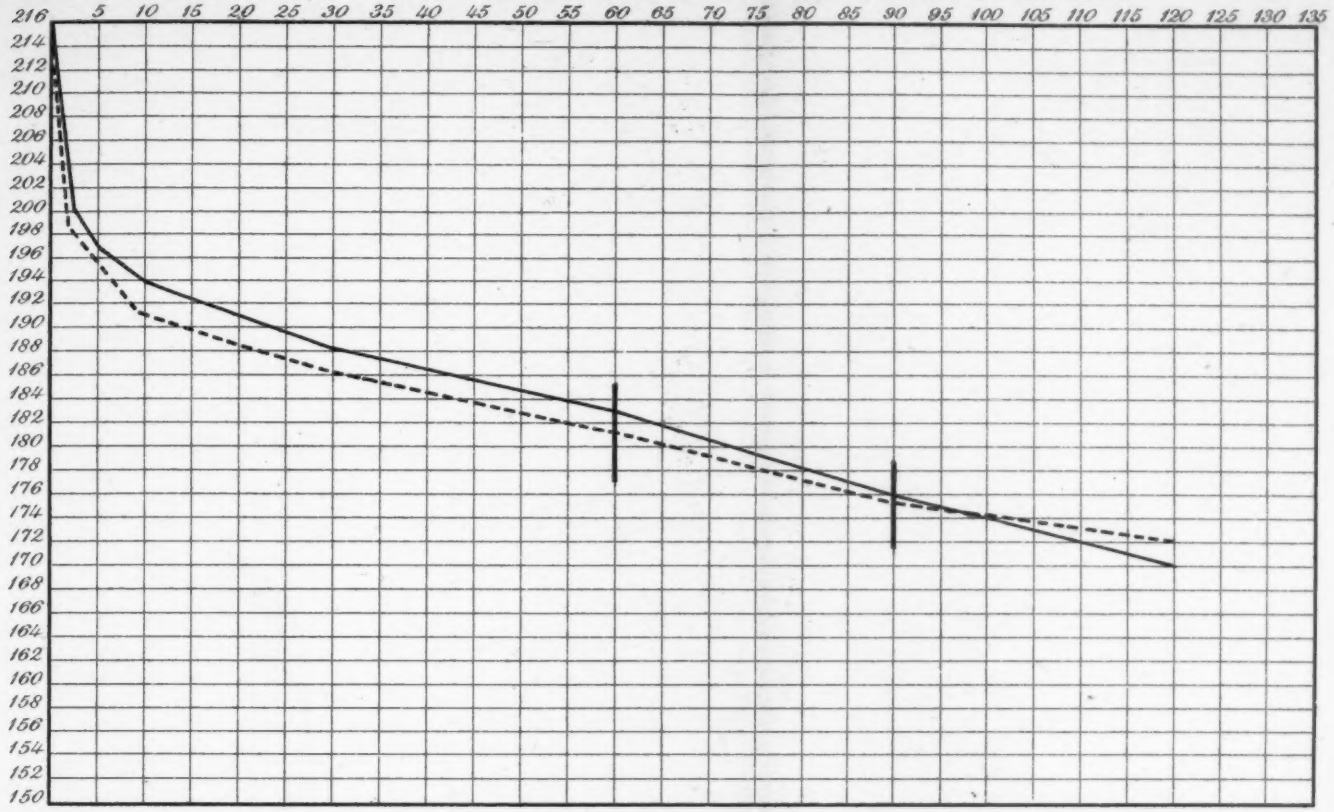

TABLE VII.

Transformations at 66° with malt-extract heated to 66° for different periods.

No. 11. Malt-extract heated to 66° for 20 minutes.
No. 12. Malt-extract heated to 66° for 40 minutes.
No. 13. Malt-extract heated to 66° for 60 minutes.
Per 100 *c.c.* 5 grms. starch. 25 *c.c.* malt-extract.
N.B.—The thick black vertical lines indicate the addition of more malt-extract.

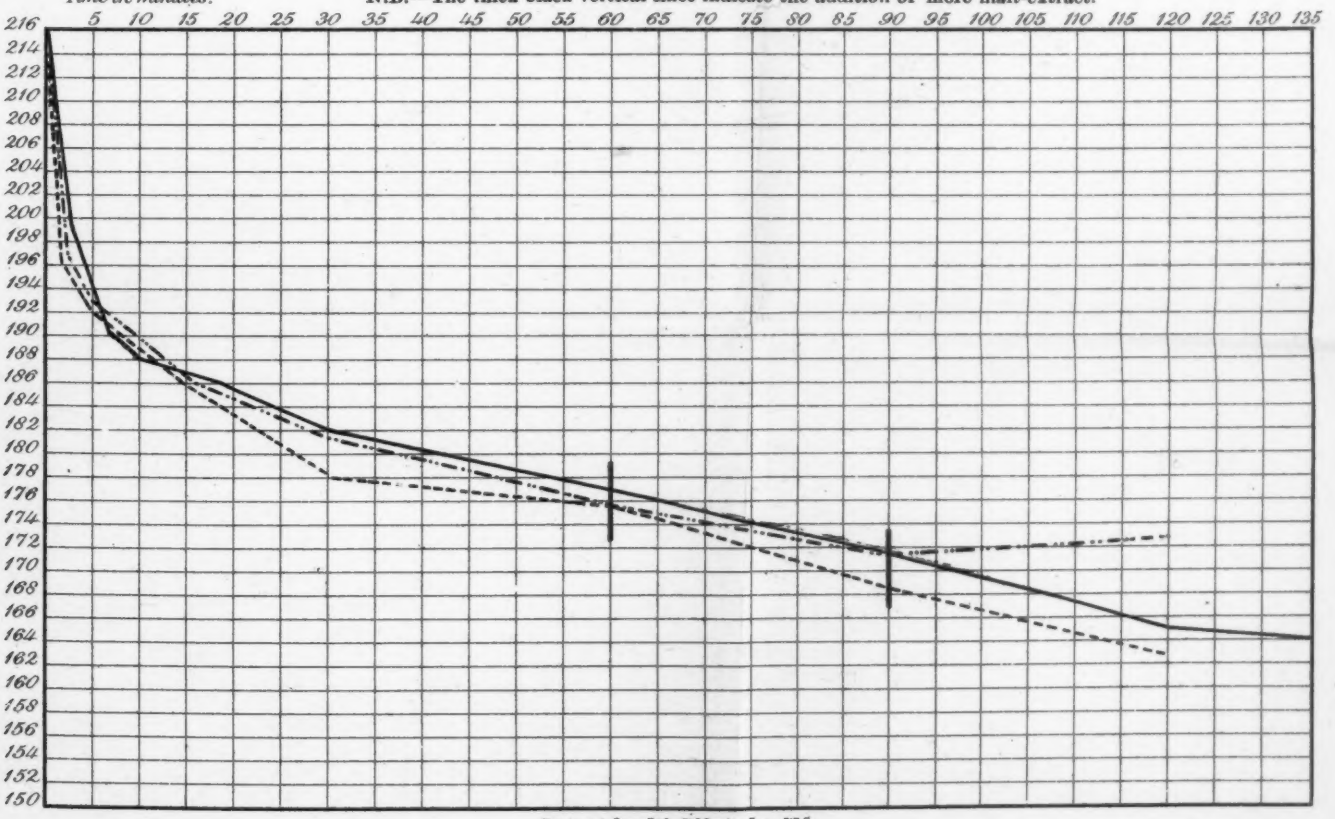

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TABLE VIII.

Transformations at 75° with malt-extract previously heated to 76° for 10 minutes

——— No. 14.
- - - - - - - No. 15. } Per 100 *c.c.* 4 grms. starch. 20 *c.c.* malt-extract.
– . – . – . – No. 16.

Time in minutes.

N.B.—The thick black vertical lines indicate the addition of more malt-extract.

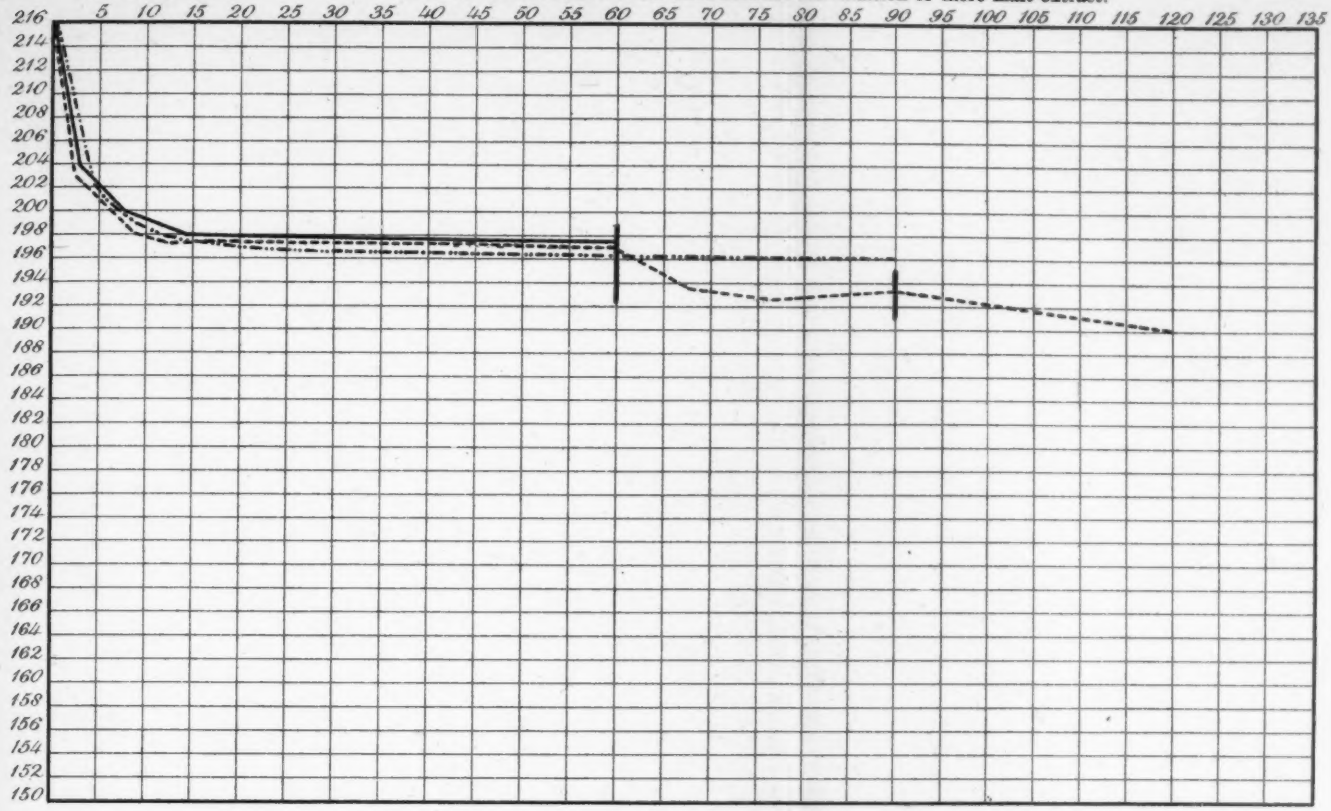

TABLE IX.

Transformations at 75° with malt-extract previously heated to 76° for 20 minutes.

——— No. 17. Per 100 *c.c.* 4 grms. starch. 20 *c.c.* malt-extract.
- - - - - - - No. 18. Per 100 *c.c.* 3·8 grms. starch. 23 *c.c.* malt-extract.

Time in minutes.

N.B.—The thick black vertical lines indicate the addition of more malt-extract.

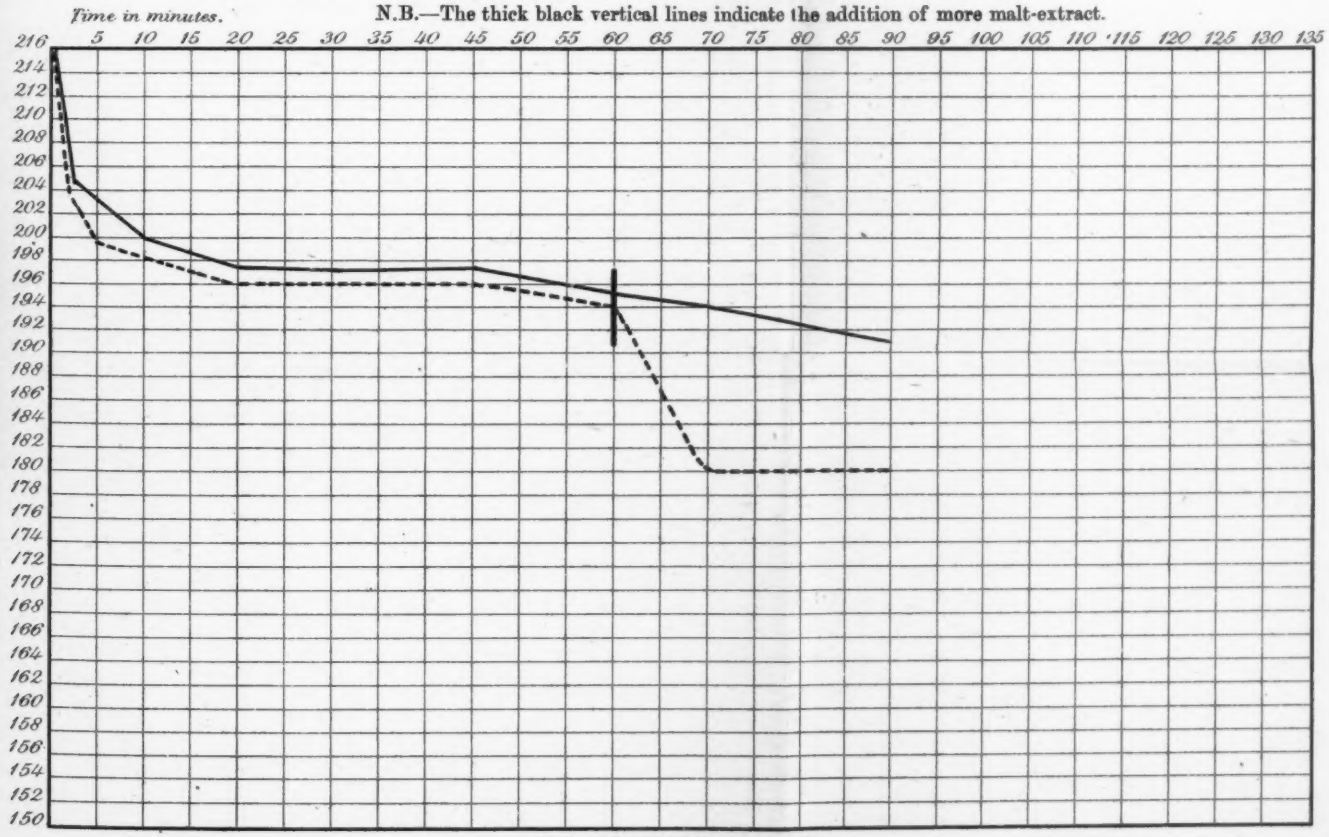

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TABLE X.

Transformations with neutralised and alkaline malt-extract.

——— No. 19. Malt-extract heated to 66° for 20 minutes, and afterwards *neutralised with* BaH_2O_2.
Per 100 *c.c.* 5 grms. starch. 16 *c. c.* malt-extract.

– – – – – No. 20. Malt-extract heated to 66°, and rendered *very slightly alkaline with* Na_2CO_3.
Per 100 *c. c.* 5 grms. starch. 19·8 *c.c.* malt-extract.

– · – · – · No. 21. Malt-extract heated to 66°, and rendered *very slightly alkaline with* Na_2CO_3.
Per 100 *c.c.* 5 grms. starch. 16 *c.c.* malt-extract.

····· No. 22. Malt-extract heated to 66°, and rendered *slightly alkaline with* Na_2CO_3.
Per 100 *c. c.* 5 grms. starch. 25 *c.c.* malt-extract.

N.B·—The thick black vertical lines indicate the addition of more malt-extract.

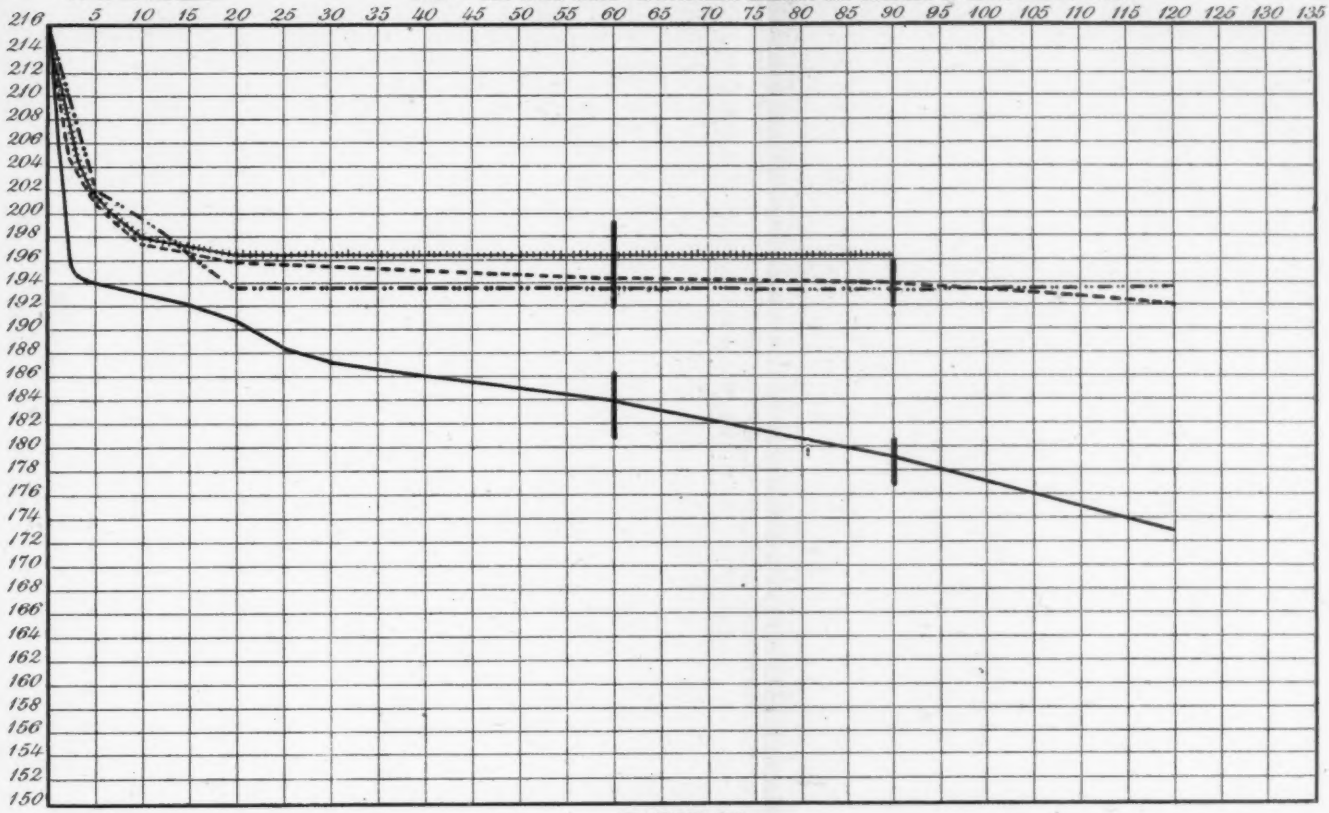

TABLE XI.

Transformation at 66° with malt-extract heated to 66°, and afterwards rendered very slightly alkaline with NaHo.

——— No. 23. Per 100 *c. c.* 5 grms. starch. 25 *c.c.* malt-extract.

N.B.—The thick black vertical lines indicate the addition of more malt-extract.

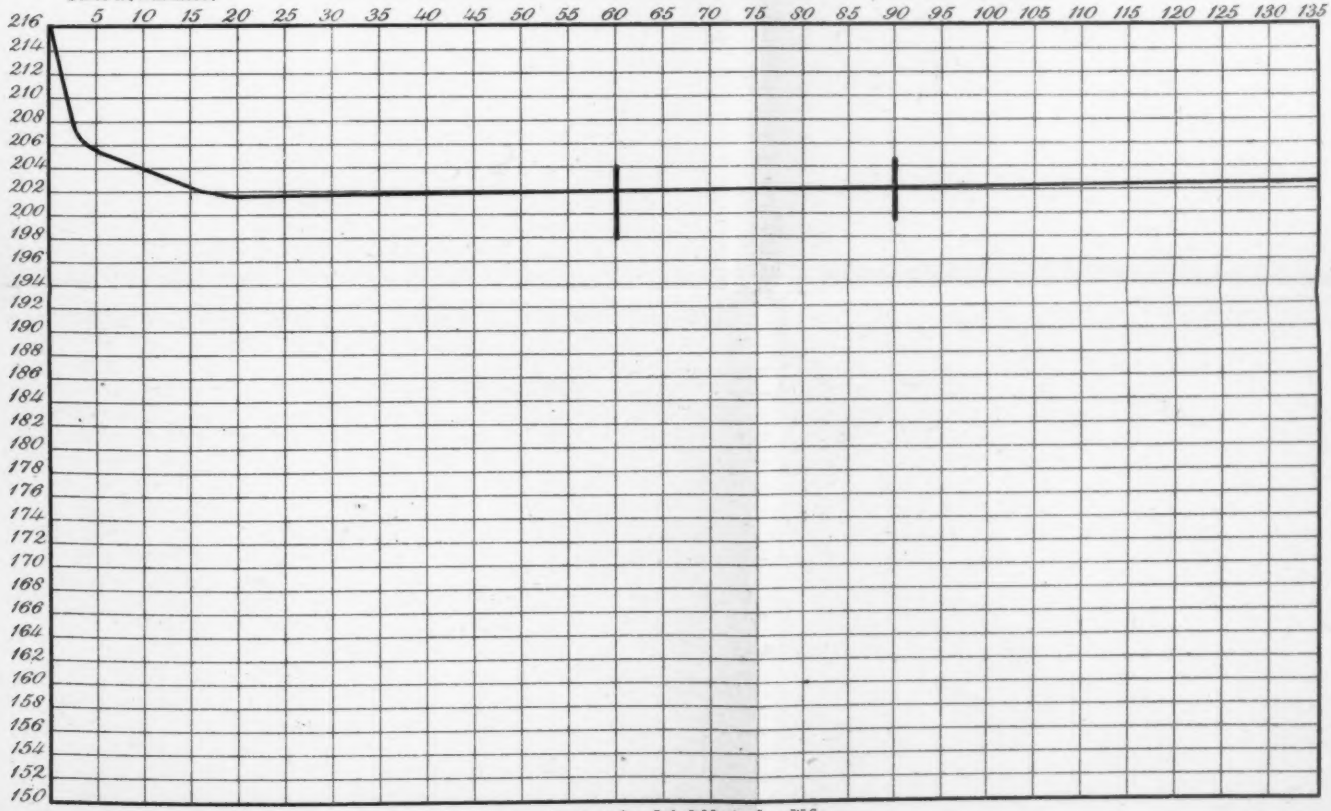

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TABLE XII.

Shewing the average curves for transformations made under different conditions.

A. Transformations with unheated malt-extract at 40°–50°.

B. Transformations with malt-extract heated to 60°.

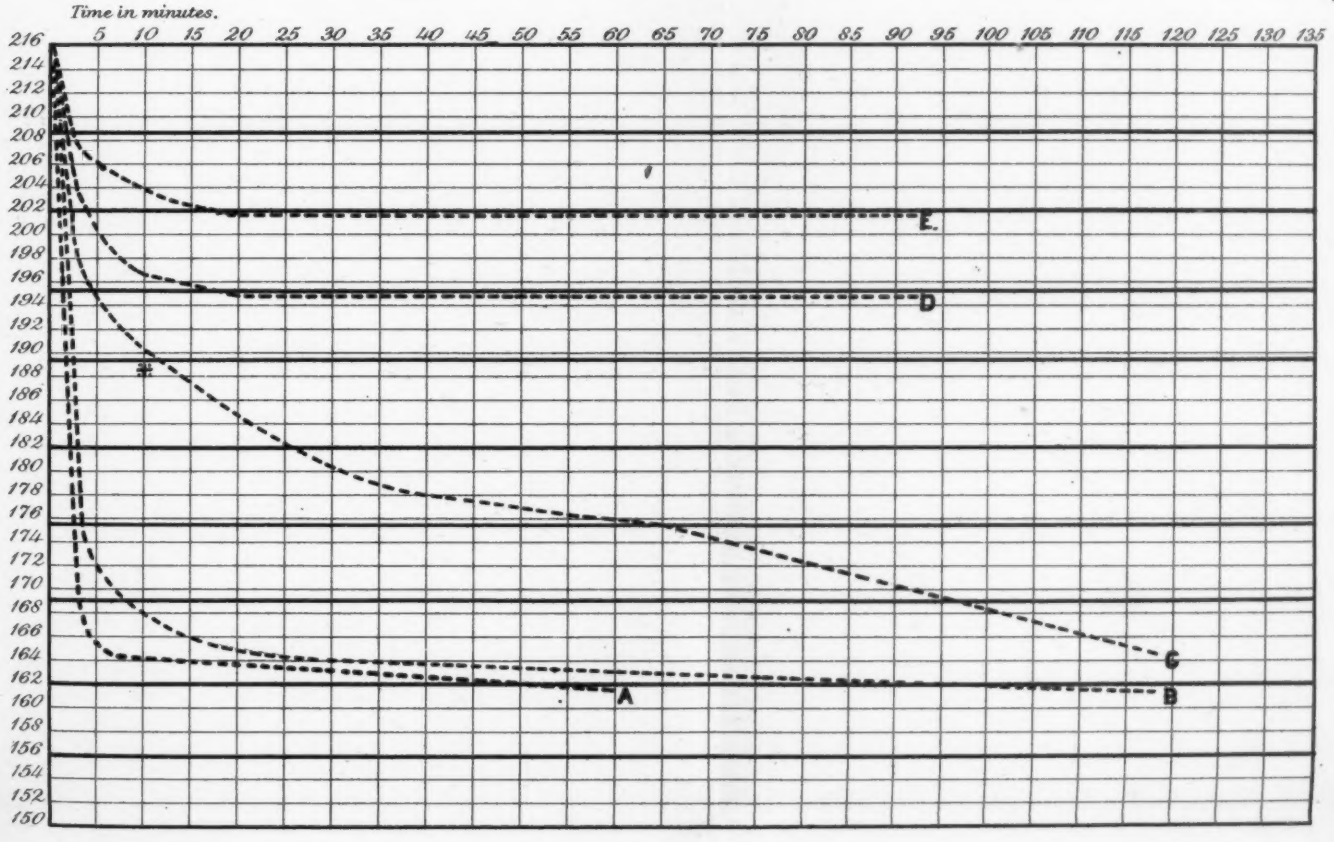
C. Transformations with malt-extract heated to 66°.

D. Transformations with malt-extract heated to 75°, and also with malt-extract heated to 66°, and rendered slightly alkaline with Na_2CO_3.

E. Transformations with malt-extract heated to 66°, and rendered very slightly alkaline with NaHo.

The horizontal thick black lines mark the position of the different theoretical transformations possible under the 10-molecule theory of the constitution of starch.

* Disappearance of iodine reaction for erythrodextrin.



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Maltose	47·3
Dextrin	52·7
	100·0

To 100 c.c. of this solution, containing about 5 grams of solid matter, were added 5 c.c. of unheated malt-extract, the temperature being at 60°.

At the end of two minutes the numbers for the starch products were found to be—

$[\alpha]_{j3\cdot86}$	162·6°
κ	49·3

corresponding to a percentage composition of

Maltose	80·8
Dextrin	19·2
	100·0

This composition was not further altered on digestion for 15 minutes longer.

In another similar experiment in which the numbers for the boiled solution were—

$[\alpha]_{j3\cdot86}$	184·2°
$\kappa_{3\cdot86}$	31·8

they were reduced by the action for two minutes of 5 c.c. of unheated malt-extract at 50° to

$[\alpha]_{j3\cdot86}$	164·4°
$\kappa_{3\cdot86}$	48·9

at which point they remained constant for some time.

If we assume that the achroo-dextrins of the higher and lower transformations are identical, there appears to be no sufficient reason why their hydration should proceed with such extreme rapidity to a certain point, and there be arrested. The phenomenon cannot be due to a weakening of the diastatic power of the transforming agent brought about by the presence of a large excess of maltose, since such a liquid is capable of readily reducing a further quantity of starch to the same point.

The explanation which most naturally suggests itself is that the dextrins are not *metameric* but *polymeric* bodies, those corresponding to transformations of high optical activity being of greater molecular complexity than those yielded by transformations of lower optical activity, the latter being produced from the former by a partial act of hydration with consequent elimination of maltose.

The separation and examination of the dextrins has confirmed this opinion.

Since arriving at these conclusions, Musculus and Gruber (*Bull. Soc. Chim.*, **30**, 69) have brought forward an identical theory to account for certain facts they have observed in connection with the action of precipitated "diastase" upon starch. They look upon starch as a polysaccharide having for its formula $n(C_{12}H_{20}O_{10})$, and undergoing under the influence of diastase and acids successive hydrations and decompositions.*

This view of the constitution of starch, or more correctly speaking, of soluble starch, we believe to be essentially correct, and quite in accordance with our experiments.

When our results are attentively considered, it will be seen that the simplest formula we can adopt for soluble starch is $10C_{12}H_{20}O_{10}$, which we may write in the following way:—

$$\left\{\begin{array}{l} C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \\ C_{12}H_{20}O_{10} \end{array}\right.$$

The first action of the transforming agent of malt-extract upon this complex and unstable molecule results in the removal by hydration of one of the groups $C_{12}H_{20}O_{10}$, thus producing maltose, whilst the remaining nine groups $C_{12}H_{20}O_{10}$ constitute the first dextrin of the series, erythro-dextrin α. This dextrin on further hydration splits up into a molecule of maltose, and erythro-dextrin β, consisting of eight $C_{12}H_{20}O_{10}$ groups. This dextrin in its turn splits up into a dextrin formed of seven such groups, which is the first achroo-dextrin.

In this way the degradation of the original molecule proceeds, until, by successive stages of hydration, maltose is reached.

The number of distinct dextrins which according to this hypothesis are possible, depend upon the molecular weight of the lowest possible dextrin. If a dextrin is capable of existing containing the same

* Dr. Armstrong has shown to one of us a proof-sheet of the forthcoming new edition of Miller's *Organic Chemistry*, printed prior to the appearance of Musculus and Gruber's paper, in which it is pointed out that the results obtained by O'Sullivan indicate that starch has a very high molecular weight, and that according as we regard dextrin as $C_{12}H_{20}O_{10}$ or $C_{24}H_{40}O_{20}$, it contains either 72 or 144 carbon atoms in its molecule.

number of carbon atoms as maltose in its molecule, nine distinct stages in the transformation may be expected; whereas if the lowest dextrin contain double as many carbon atoms as maltose, there can only be eight.

The following table represents the value of $[\alpha]_{j3\cdot86}$ and $\kappa_{3\cdot86}$ for the joint products of each of the theoretical transformations, the resulting dextrins being given in the second column :—

No. of transformation.	$[\alpha]_{j3\cdot86}$.	$\kappa_{3\cdot86}$.	Resulting dextrin.
Soluble starch	216·0°	0	—
(1)	209·0	6·4	Erythro-dextrin α
(2)	202·2	12·7	,, β
(3)	195·4	18·9	Achroo-dextrin α
(4)	188·7	25·2	,, β
(5)	182·1	31·3	,, γ
(6)	175·6	37·3	,, δ
(7)	169·0	43·3	,, ϵ
(8)	162·6	49·3	,, ζ
(9)	156·3	55·1	,, η
Maltose	150·0	61·0	—

Of these possible transformations our experiments have unmistakeably established the existence of Nos. (2), (3), (4), and (8), whilst indications of (5) and (6) have been frequently obtained in various ways, but not with the same amount of certainty as in the other cases.

The dextrins corresponding to Nos. (1) and (2) are erythro-dextrins, all the others being achroo-dextrins.

By far the most stable dextrin is that of transformation (8). Between this point and the complete hydration to maltose we have been unable to determine any indication of a slackening of the reaction, which fact appears to favour the second of the views above expressed. It is true that transformation (9) can be obtained by continuing the digestion of (8) for some time with unheated malt-extract, but the fall in angle is continuous and regular until maltose is reached.

Throughout the whole range of the transformations of starch, conducted with malt-extract under the most varying conditions, the results obtained have always been compatible with the hypothesis that the hydration* and splitting up of the molecule of soluble starch are

* Dr. H. E. Armstrong has suggested the appropriate term *hydrolysis* to denote the assimilation of the elements of water with a simultaneous splitting up of the molecule; *hydration* being used to denote merely the fixation of the elements of water unattended by any splitting up of the resulting molecule.

The conversion of starch into maltose and dextrin, and the inversion of cane-

attended with the production of (1) a crystallisable body, *maltose*, having a specific rotatory power of $[\alpha]_j$ 150°, and a cupric oxide reducing power of 61, and (2) of a series of non-crystallisable polymeric bodies, the dextrins, having all the same specific rotatory power of $[\alpha]_j$ 216°, and no reducing power.

Musculus has stated that the different dextrins have a varying action on polarised light, and are all capable in a different degree of reducing cupric oxide. If this statement is assumed to be correct, it is evident that the values of $[\alpha]_j$ and κ for the dextrins must throughout the series vary inversely, and in such a manner that these bodies may be looked upon as mixtures or combinations of maltose with a dextrin of $[\alpha]_j$ 216°, and no reducing power. Such a view has been taken throughout the course of this paper.

We are at present engaged with the isolation and study of the different dextrins, a work promising results of great interest, which we hope to communicate to the Society at a comparatively early date.

Is Dextrose a Product of the Action of Malt-extract upon Starch?

In order to arrive at an answer to this important question, we have investigated the result of prolonged action of considerable quantities of malt-extract upon a solution of dextrin-maltose of known composition.

In these experiments the greatest possible care was taken to ensure that the duplicate samples of malt-extract were treated in an exactly similar way to the transformation liquids themselves.

Experiment I.—A solution of the transformation products was obtained in the ordinary way, having the following properties:—

$[\alpha]_{j3\cdot86}$	163·6°	Maltose	80·1
$\kappa_{3\cdot86}$	48·9	Dextrin	19·9
			100·0

To 75 c.c. of this solution were added 25 c.c. of malt-extract previously heated to 62°. The mixture was digested for 16 *hours* at 55°, when the corrected starch-products yielded the following results:—

$[\alpha]_{j3\cdot86}$	152·1°	Maltose	97·8
$\kappa_{3\cdot86}$	59·6	Dextrin	2·2
			100·0

sugar, are examples of ***hydrolytic action***; whilst the conversion of ethylene oxide into glycol is an instance of ***hydration***.

Experiment II.—A starch conversion at 60° C. with malt-extract heated to 62°; time of conversion 1 hour—

$[\alpha]_{j3\cdot86}$ ..... 164·0°
$\kappa_{3\cdot86}$ ..... 49·57

This solution after boiling was divided into three portions, A, B, and C.

A. 74·5 c.c. digested with 25·5 c.c. of unheated malt-extract for 16 hours at 53° C.

Starch-products corrected.

$[\alpha]_{j3\cdot86}$ ..... 147·0°
$\kappa_{3\cdot86}$ ..... 61·5

B. 74·6 c.c. digested with 25·4 c.c. of malt-extract (previously heated to 62°) for 16 hours at 53° C.

Starch-products corrected.

$[\alpha]_{j3\cdot86}$ ..... 150·5°
$\kappa_{3\cdot86}$ ..... 58·3

C. 74·5 c.c. digested with 25·5 c.c. of *boiled* malt-extract for 16 hours at 53° C.

Starch-products corrected.

$[\alpha]_{j3\cdot86}$ ..... 166·0°
$\kappa_{3\cdot86}$ ..... 49·3

In this last experiment, No. II, in order to obtain all the corrections for the malt-extract, it was necessary to make a separate analysis—

(1.) Of the malt-extract heated to 62° and digested for one hour at 60°.

(2.) Of No. (1) after raising to the boiling point.

(3.) Of unheated malt-extract after digestion for 16 hours at 53°.

(4.) Of malt-extract heated to 62° and digested for 16 hours at 53°.

(5.) Of malt-extract boiled and digested for 16 hours at 53°.

It is only by taking these precautions when dealing with such a changeable body as malt-extract, that results of any accuracy can be obtained.

In the following experiments the malt-extract was added in successive portions at different periods of the digestion, instead of only at the commencement.

Experiment III.—A solution of transformation products prepared, giving, when corrected—

$[\alpha]_{j3\cdot86}$ ..... 162·3°
$\kappa_{3\cdot86}$ ..... 49·6

75 c.c. of this solution on digestion at 50° for 16 hours with 24·7 c.c. of malt-extract, added at three different periods, gave for the corrected starch products—

$[\alpha]_{j3\cdot86}$ ..... 147·7°
$\kappa_{3\cdot86}$ ..... 60·8

Experiment IV.—*Original Starch-products.*

$[\alpha]_{j3\cdot86}$ ..... 164·3°
$\kappa_{3\cdot86}$ ..... 48·5

66 c.c. of this solution were digested with 34 c.c. of malt-extract for 28 hours, the malt-extract being added in four different portions.

Starch-products corrected.

$[\alpha]_j$ ..... 148·2°
κ ..... 58·6

All the foregoing experiments prove most conclusively that *no dextrose is formed* by the prolonged action of malt-extract upon starch. The final product of the reaction is *maltose*, which, as we have previously shown, is not further hydrated either by the transforming agent itself, or by the small amount of acid contained in the malt-extract. The apparent production of dextrose in the experiments of other observers has resulted partly from the non-observance of the precautions we have shown to be so necessary, and partly from the fact that the cupric oxide reducing power of maltose has been hitherto taken at too high a value.

The Nature of Diastase.

When malt-extract is gradually heated coagulation is first apparent at about 46° C.

When this temperature is maintained, the maximum amount of precipitation possible under these conditions takes place in from 15 to 20 minutes, a continuance of the heating having no further influence. If, however, the temperature is raised a few degrees, a further coagulation takes place, which in turn soon attains a maximum. This increase of coagulation with the temperature continues up to about 95° C.

The amount of coagulation produced by heating equal quantities of normal malt-extract to a given temperature, is shown in the following table. The third column gives the quantity of precipitated albumin calculated as a percentage upon the total amount thrown down at 100°.

100 *c.c. of Normal Malt-extract.*

Temperature.	Grams of albumin coagulated.	Percentage of total amount.
50°	0·044	19·1
60	0·123	53·5
66	0·155	67·4
76	0·186	80·8
100	0·230	100·0

Every stage in the coagulation of malt-extract by heat is attended with a distinct modification of its starch-transforming power; and, conversely, we have never been able to discover any modification in starch-transforming power which is not attended with distinct coagulation.

In addition to this, at 80—81°, the point at which the diastatic power of malt-extract is destroyed, nearly the whole of the coagulable albuminoïds have been precipitated. We are consequently led to conclude that the diastatic power is a function of the coagulable albuminoïds themselves, and is not due, as has been generally supposed, to the presence of a distinctive transforming agent.

This supposition is rendered still more probable from the following considerations.

When malt-extract is filtered once or twice under slight pressure through a thin porcelain diaphragm, such for instance as that afforded by a porous battery cell, we find that the filtrate, on being heated to the boiling point, throws down no albuminoïds, but only a trace of calcic phosphate. This phenomenon is doubtless due to the same cause as that described when calling attention to the properties of soluble starch treated in a similar manner. The albuminoïds being highly colloïdal, and having a large "solution molecule," refuse to pass through the diaphragm.*

* These results have an important bearing upon the experiment first described by Dr. W. Roberts, which has been frequently quoted as affording a most powerful argument against the doctrine of abiogenesis. This observer found that on filtration of a vegetable infusion, swarming with bacteria, through porous earthenware, the filtrate, when placed under conditions of temperature favourable to the production of organisms, remained barren and unchanged; a result which was attributed entirely to the separation of the bacteria and their germs.

We now see, however, that the liquid may have been modified very considerably by such a treatment, the albuminoïds or plastic material upon which the heterogenists rely for the spontaneous production of life, being partially or entirely removed.

It must not be considered that we are in any way advocates of the doctrine of abiogenesis, which we consider opposed to a great mass of trustworthy evidence. We wish merely to point out that this so-called *experimentum crucis* of Dr. Roberts by no means possesses the value which is commonly attributed to it.

We have been unable to discover any alteration in the composition of malt-extract so treated, except this loss of albuminoïds; it is true that the dextrorotatory power of the liquid increases somewhat, but this is entirely due to the separation of the lævorotatory albumin.

When the action of the filtrate is tried upon starch-paste it is found to possess *absolutely no transforming power. It has lost all diastatic action as fully and completely as if it had been heated to the boiling point.*

In this case, without the application of heat, removal of the coagulable albuminoïds has again been attended with loss of transforming power. Diastatic action appears to be as inseparably connected with the coagulable albuminoïds as the production of alcohol is with the yeast-cell, and the evidence in favour of a causal connection of these phenomena appears to us to be as strong in the one case as in the other.

Barley before germination contains more soluble coagulable albuminoïds than after the malting process is completed. The following table gives the results obtained by coagulating at different temperatures equal quantities of *normal* aqueous barley-extract. The barley was similar to that used after germination in the last experiment of the kind, 100 parts of barley being used for the preparation of the extract instead of 80 parts of malt.

100 *c.c. of Normal Barley-extract.*

Temperature.	Grams of albumin coagulated.	Percentage on total quantity precipitated at 100° C.
50°	0·063	18·3
60	0·194	56·5
66	0·233	67·9
76	0·311	90·6
100	0·343	100·0

Although the actual amount of coagulable albumin is considerably greater in barley than in malt, the percentage of the total amount precipitated at the same temperature in each case is very similar.

The coagulable albuminoïds of fresh barley-extract, although to all appearances differing but little from those of malt-extract, possess but very feeble diastatic power. Those portions which are coagulated only at temperatures above 66° are without action upon starch-paste, whilst those precipitated at temperatures below 66° have a feeble action, which, however, is probably only from $\frac{1}{50}$ to $\frac{1}{100}$ of the intensity of those existing in solution in malt-extract at the same temperature.

During the process of germination the coagulable albuminoïds must evidently undergo some change, which, without materially altering

their physical properties, confers upon them a large amount of potential energy.

It is possible that these bodies consist of portions of the cell-protoplasm (still retaining some of the properties of living protoplasm) which are thrown into a state of varying molecular tension whilst undergoing the modifications necessary for the requirements of the growing embryo. The direction of these modifications is probably from the extreme colloïdal form to a state admitting of freer passage through the cell-walls.

The molecular tension of the albuminoïds results in great instability of composition, which is capable, under favourable conditions, of inducing the hydrolysis of starch.

We have up to the present time been unable to discover any marked change of state in the transforming agent attendant upon the liberation of so large an amount of energy. It is evident that some such change must take place, but it has hitherto escaped our notice.

It is possible to augment the transforming power of the comparatively inactive albuminoïds of barley after their separation from the grain, and, consequently, without the aid of germination. An aqueous extract of barley, which is submitted for a few hours at a temperature of 30° C. to the action of ordinary yeast, has its power of transforming starch much increased by this treatment. A mixture of yeast and pure cane-sugar placed under identically the same conditions, affords a liquid which does not possess the slightest action upon starch. It is evident that the growing yeast-cell is capable of inducing certain modifications in the albuminoïds which, during the ordinary process of germination, are brought about by the action of the living vegetable cell itself.

This curious action appears to be confined to the saccharomyces. Whenever schizomycetes only are present in the barley-extract, the infusion, far from gaining in diastatic power, rapidly loses that which it originally possessed.

We believe that a combination of the broad principles of Liebig's theory of fermentation with a portion of Frémy's hypothesis of "hemi-organisation" (*vide* "Sur la Génération des Ferments") will prove capable of connecting coherently all the known facts of the so-called *diastatic fermentations*.

On the above hypothesis, the influence of heat upon the subsequent action of malt-extract upon starch becomes more comprehensible than heretofore.

The first action of heat is to destroy by "heat-stiffening" those modifications of the cell-protoplasm which, during their action, liberate a large amount of energy, sufficient to effect the hydrolysis of the smaller and more stable molecules of the dextrins low in the

series. As these more active bodies are gradually reduced in quantity by an increase of temperature, the albuminoïds still remaining uncoagulated are those which are capable of liberating a comparatively small amount of energy, which, although still sufficient to hydrolyse the more complex and less stable molecules of the higher dextrins, is insufficient to effect any change in the more stable molecules of the lower dextrins.

Unlike the organised ferments, the diastatic ferments do not possess any power of reproduction, consequently their transforming action is limited, and strictly proportional to the amount of transforming agent present. This being the case, the relative transforming powers of any two infusions of malt may be readily ascertained by conducting two transformations of starch under identically similar conditions, and constructing in each case a time-curve similar to those described. The relative energy of transformation is measured by the amount of degradation of the starch in a given time.

LXVI.—*On the Action of Hydrochloric Acid on Manganese Dioxide.*

By Spencer Umfreville Pickering, Brackenbury Scholar of Balliol College, Oxford.

A short time ago attention was drawn to this subject by a paper which appeared in the September number of this Journal for 1878, by W. W. Fisher, entitled "On Manganese Tetrachloride," in which the author stated that it was this body which was produced by the action of cold concentrated hydrochloric acid on either the dioxide, sesquioxide, or red oxide of manganese. After a careful perusal of this paper, it appeared to me that however correct the author's experiments on the subject might be, the conclusions which he drew from them were open to discussion.

It is there stated that when the dark-brown liquid obtained by dissolving any of the three higher chlorides of manganese in cold strong hydrochloric acid, is diluted with a large quantity of water, it deposits a precipitate of the hydrated dioxide, and that for each atom of manganese thus precipitated there is a disappearance of two atoms of available chlorine from the liquid, *i.e.*, of chlorine that will liberate iodine when treated with potassium iodide. The author hence concludes that each molecule of the higher chloride present in the liquid before precipitation consists of an atom of manganese combined with

four atoms of chlorine, two of which atoms are retained but loosely; or, in other words, that the higher chloride is $MnCl_4$, and that its decomposition by water and by potassium iodide takes place according to the two following equations:—

$$\text{I.} \quad MnCl_4 + 2H_2O = MnO_2 + 4HCl.$$
$$\text{II.} \quad MnCl_4 + 2KI = MnCl_2 + 2KCl + I_2.$$

But it is perfectly possible that the manganese dioxide precipitated in the first case may bear precisely the same ratio to the iodine liberated in the second case, if, instead of being $MnCl_4$ the higher chloride is Mn_2Cl_6, or, indeed, any chloride corresponding to the general formula Mn_nCl_{2n+2}; the reactions, in the case of the sesquichloride for instance, being represented by the equations—

$$\text{III.} \quad Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl,$$
$$\text{IV.} \quad Mn_2Cl_6 + 2KI = 2MnCl_2 + 2KCl + I_2,$$

these equations only differing from those given above by the addition of $MnCl_2$ to both sides in each case; and as no attempt was made to ascertain how much of the large excess of manganous chloride present in the liquids, together with the higher chloride, was necessary to the existence of this latter, and took part in the reactions above given, these experiments afforded no proof whatever that the higher chloride of manganese was $MnCl_4$ and not Mn_2Cl_6 or Mn_3Cl_8. The only argument which is adduced to show the non-existence of the two last-mentioned chlorides is, that in the case of the sesquioxide, its solution by hydrochloric acid cannot be supposed to take place in the following way:

$$\text{V.} \quad Mn_2O_3 + 6HCl = Mn_2Cl_6 + 3H_2O,$$

because the oxide, precipitated from the solution thus obtained, is the dioxide and not the sesquioxide, and that, therefore, it must take place according to the equation—

$$\text{VI.} \quad Mn_2O_3 + 6HCl = MnCl_4 + MnCl_2 + 3H_2O,$$

recognising the possibility of a chloride corresponding to the dioxide being obtained from the sesquioxide, but denying the possibility of the dioxide being obtained from a chloride corresponding to the sesquioxide. By a precisely similar method of reasoning, the author argues that when the oxide, Mn_3O_4, is treated with hydrochloric acid, it does not form the corresponding chloride, Mn_3Cl_8, but $MnCl_4$.

Besides performing a number of original experiments on the subject, I have repeated all those made by Fisher with the greatest possible care. The main points in his paper are as follows:—

(1.) That from the liquid containing the higher chloride water always precipitates a definite substance.

(2.) That this substance is always manganese dioxide.

(3.) That the ratio which the manganese precipitated bears to the loosely combined chlorine of the higher chloride from which it is precipitated, is as 1 : 2 atoms.

(4.) That this higher chloride is $MnCl_4$.

The experiments detailed below will, I think, prove conclusively—

(1.) That from a solution of manganese dioxide in cold hydrochloric acid water does not precipitate a definite substance.

(2.) That the substance precipitated is not manganese dioxide, but a mixture of the dioxide with the sesquioxide in variable proportions.

(3.) That the ratio which the precipitated manganese bears to the available chlorine of the chloride from which it is precipitated, is not 1 : 2 atoms.

(4.) That the higher chloride produced is not $MnCl_4$, but, in all probability, Mn_2Cl_6.

§ I. *Substances used.*

As all attempts at purchasing a sample of pure manganese dioxide were unsuccessful (the best specimen obtained containing only 35 per cent. of the dioxide, the remainder consisting of sesquioxide), a solution of this oxide in hydrochloric acid was made, and then diluted with a large volume of water, relying on Fisher's statement that in this way pure manganese dioxide is precipitated; but, unfortunately, since this statement is incorrect, the body thus obtained was not the dioxide, but, after being washed and dried at a temperature below 100° C., it yielded the following numbers on analysis:—

	A.		B.	
$MnO_2 \left\{ \begin{matrix} 85{\cdot}259 \\ 85{\cdot}039 \end{matrix} \right\} = 85{\cdot}149$			85·149	
MnO	9·362	(determined directly by total manganese)	9·360	(by difference)
H_2O	5·489	(by difference)	5·491	(determined directly)
	100·000		100·000	

The substance, therefore, corresponds to a mixture containing 78 per cent. of the dioxide and 22 per cent. of the sesquioxide.

Seeing that Wright and Luff (*Chem. Soc. J.*, 1878, 513) did not succeed in their endeavours to obtain pure manganese dioxide by two of the ordinary processes given for its preparation, no more time was spent in attempts to procure this substance, but the sample, the analysis of which is given above, was employed in the following ex-

periments, the 9 per cent. of protoxide which it contained being allowed for in calculating out the results wherever necessary.

As in the above analysis, so I shall throughout this paper, both for the sake of clearness of expression as well as to simplify the calculations, consider the sesquioxide and the red oxide as mixtures of the dioxide and protoxide, although, no doubt, under none of the given circumstances could the protoxide exist as such, still, this will introduce no error whatever into the deductions from the experiments, since the sesquioxide reacts with hydrochloric acid, potassium iodide, and other reagents, precisely as a mixture of an equal number of molecules of the dioxide and protoxide would, and the red oxide in the same manner as a mixture of one molecule of the dioxide to every two of the protoxide.

The hydrochloric acid used possessed a density of 1·1958 at 15° C., = 39·114 per cent. HCl.

Except where otherwise stated the proportions employed were 50 mols. of the acid to every 1 mol. of the dioxide, or 44·5 c.c. of the aqueous acid to every 1 gram of pure dioxide taken: a smaller proportion of acid would have been sufficient, but this large excess was used because it was found to be advantageous in most cases to effect the solution with rapidity.

§ II. *Preliminary Experiments.*

When manganese dioxide is treated with cold hydrochloric acid some chlorine is evolved at once, the oxide dissolving more or less rapidly according to the strength of the acid employed, to form a very dark-brown opaque liquid. The solution thus obtained decomposes slowly at ordinary temperatures, evolving chlorine, and ultimately leaves a liquid containing nothing but manganese dichloride together with any excess of acid which may have been employed; this change, however, takes a considerable time to complete itself, and I have at the present moment a solution of the dioxide in hydrochloric acid, which, although it has been exposed to the air in an open beaker for the last four weeks, still smells slightly of chlorine, and is sufficiently dark in colour to show that the whole of the higher chloride originally present in the liquid is not yet entirely decomposed. Heat favours the decomposition, though, even at the boiling point of the solution, it takes some five or ten minutes to become complete. When the solution is effected in a sealed tube, the same phenomena as those above described are observed, though experiments have not been carried on for a sufficiently long time to enable me to state whether the solution is ultimately decomposed or not; at any rate, if such is the case, it does not take place within four months at ordinary temperatures. If the sealed tube with its contents is heated to 100° C. it soon becomes suffi-

ciently light in colour to be slightly transparent, but even prolonged heating at this temperature is incapable of producing total decomposition. When the heated liquid is cooled, it does not regain its original dark colour, showing that the chlorine when once liberated in incapable of recombining with the constituents of the solution to form the more highly chlorinated compound from which it was evolved.

When the dark liquid, obtained as above described, is cautiously diluted with water, a large quantity of the latter (5 or 6 volumes) may be added without causing any decomposition; but, on further increasing the quantity added, the liquid suddenly becomes turbid, depositing a dark, or sometimes rather light brown precipitate, the precipitation of which becomes complete in a very few minutes: the deposition of this body is effected more quickly by pouring the solution of the chloride into a large volume of water instead of adding the water gradually to the chloride. A moderate heat facilitates and increases the precipitation, as well as causing a further precipitation to take place in the cold diluted solution which still contains some of the higher chloride undecomposed. With the proportions of oxide and acid above mentioned, namely, 1 mol. of the former to 50 mols. of the latter, as well as when the proportion of manganese is increased to three or four times this quantity, the decomposition is complete when 20 volumes of water are used for each volume of the acid solution taken; with only 10 volumes the decomposition is nearly complete (about 96 or 97 per cent.), but not entirely so. That the precipitation is complete with 20 volumes of water was ascertained in the following ways: by seeing whether the further addition of water produced any further precipitation, whether the diluted liquid remained perfectly clear on being warmed, and, lastly, by freeing the acid solution (before being diluted) from all uncombined chlorine, with the exception of a minute trace, diluting with water, and ascertaining whether the filtrate liberated more than a trace of iodine from potassium iodide; the quantity actually found in this way, and with these proportions, was quite inestimable, consequently the precipitation is rendered, for all practical intents and purposes, quite complete by the addition of 20 volumes of cold water, and this is the proportion used in every case, except where otherwise stated.

The phenomena exhibited by the action of hydrochloric acid on both the sesquioxide and the red oxide, as well as the reactions of the solutions thus obtained, are precisely similar to those exhibited in the case of the dioxide, with the exception of this one particular—that the dioxide under no conditions will dissolve without the simultaneous liberation of a considerable quantity of chlorine, whereas the two other oxides may do so without the liberation of any. The reason of this difference will be fully explained below.

§ III. *The Substance Precipitated.*

After the preliminary experiments above alluded to had been performed, the first point which it appeared desirable to ascertain was, the nature of the substance precipitated by water from the solution of the dioxide in hydrochloric acid.

A few simple experiments soon showed that it was impossible to estimate manganese with any attempt at accuracy by igniting its oxides and weighing as Mn_3O_4; the composition of the substance thus obtained being very variable, depending on the temperature and on the tension of the oxygen of the atmosphere in which the ignition is made, as was first pointed out by Dittmar in 1865 (this Journal, p. 294). The following method of analysis was therefore adopted.

An unweighed portion of the oxide was treated with hydrochloric acid in the presence of potassium iodide, and the liberated iodine determined by means of sodium thiosulphate; the whole of the manganese was then precipitated by potash, and the precipitate, after being washed, dried, and ignited, was weighed, and the excess of oxygen over that present as MnO titrated by iodine.* These determinations gave the relative amounts of manganese dioxide and total manganese contained in the substance.

A number of experiments on the subject showed that the manganese dioxide contained in the moist precipitates, when heated, even to 100°, lost some of its oxygen, and that the sesquioxide contained in them, when heated to the same temperature, absorbed oxygen; both these reactions increasing in extent up to 200° or 250°. These experiments, the details of which I hope shortly to bring before this Society, proved clearly that the analysis of the precipitated oxides after being dried by the aid of heat, would afford no evidence as to their composition when first precipitated, and, as no means for their desiccation *in vacuo* were available, they were analysed in the moist state.

The substance which is precipitated by water from a solution of the higher chloride of manganese is a mixture of oxides, approaching in composition to the dioxide, but never consisting of this latter oxide alone, or at least in the eighteen or twenty analyses made of it, it was never found to do so; nor is it even constant in composition, but varies between the formula, $16MnO_2$, $5MnO$, and $36MnO_2$, $5MnO$, or, between $11MnO_2$, $5Mn_2O_3$, and $31MnO_2$, $5Mn_2O_3$. The conditions of the precipitation were varied in different ways: by using water at different temperatures and in different quantities, by freeing the acid liquid from chlorine before dilution, by causing only a partial precipi-

* Unknown to the author, Wright and Luff had previously adopted this method of determining manganese.

tation, by using a solution containing a large or small excess of acid, and finally, by diluting with a solution of sodium acetate instead of water. Fisher having preferred using a solution of this salt to water for reasons to be discussed hereafter. No relations, however, could be traced to exist between the composition of the precipitate and the circumstances under which it is precipitated, nor with the variation in the depth of its colour.

Some of the analyses thus obtained are given in Table I. Except where otherwise stated, the proportion to manganese dioxide used to the hydrochloric acid in which it was dissolved was 1 : 17 mols., or 3 grams of the former to 50 c.c. of the latter. In this table columns 2 and 3 give the analytical numbers obtained; columns 4 and 5, the ratio which the manganese precipitated as monoxide bears to that

TABLE I.—*Showing the Composition of various Precipitates obtained.*

1.	2. MnO_2.	3. Total Mn.	4. Mn as MnO.	5. Mn as MnO_2.	6. Conditions of the Precipitation.
	gram.	gram.			
1.	0·3016	0·2405	1	3·84	8 vols. cold water added gradually. Decomposition of the chloride very incomplete.
	0·2939	0·2384	1	3·52	
2.	0·3106	0·2253	1	6·77	Poured into 10 vols. cold water. Decomposition not quite complete.
3.	0·3123	0·2326	1	5·61	Poured into 20 vols. cold water.
	0·2834	0·2122	1	5·40	
4.	0·2900	0·2326	1	5·86	Poured into 50 vols. cold water.
	0·3133	0·2317	1	5·99	
5.	0·2947	0·2256	1	4·73	Poured into 100 vols. cold water.
6.	0·2934	0·2391	1	3·45	Same as No. 5.
	0·2769	0·2298	1	3·19	
7.	0·3230	0·2327	1	7·14	Poured into 20 vols. cold water.
8.	0·2867	0·2071	1	7·00	,, ,, hot ,,
	0·2906	0·2091	1	7·22	
9.	0·2961	0·2290	1	4·46	Same as No. 8.
	0·2989	0·2343	1	4·15	
10.	0·3122	0·2481	1	3·89	Poured into 20 vols. of a cold 10 per cent. sodium acetate sol.
	0·2828	0·2244	1	3·91	
11.	0·3069	0·2232	1	6·5	Poured into 20 vols. of a cold 5 per cent. sodium acetate sol.
12.	0·3007	0·2191	1	6·52	Same as No. 3, but the acid liquid containing only half as much of the higher chloride.
	0·2789	0·2015	1	6·99	
13.	0·3201	0·2330	1	6·60	Same as No. 3, but the acid liquid containing twice as much of the higher chloride.
	0·3216	0·2335	1	6·73	
14.	0·2822	0·2175	1	4·56	Same as No. 3, but the liquid nearly freed from chlorine before dilution.
	0·2970	0·2321	1	4·23	
15.	0·2864	0·2111	1	6·01	Same as No. 14.

precipitated as dioxide; and column 6, the conditions under which the precipitation was effected.

The next question which suggested itself was, whether the mixture of oxides thus obtained by the decomposition of the higher chloride of manganese by water, was really formed in the first instance, or whether it did not owe its variable and indefinite composition to some secondary reaction taking place after the precipitation, and before the liquid could be separated from the precipitate. That no secondary action modified the constitution of the precipitate was proved beyond doubt, though it will be well to defer giving the details of this proof till § VI.

It is now possible to give some of the reasons which led to Fisher's statement that the substance precipitated in this reaction was the pure dioxide. In the first place, he dried the precipitates obtained at 180° C., assuming that their composition, so far as regarded manganese and oxygen, would remain unaltered during this process, whereas the experiments alluded to above (p. 659) clearly showed that this was by no means the case: secondly, it was apparently presumed that by heating these precipitates at 180°, till their weight remained constant, they had necessarily been deprived of all the water which they contained; experiments on this point, however, proved that these substances, even when dried at 200°, still retained from 3 to 6 per cent. of moisture. When, to these various sources of inaccuracy we add, that a very uncertain method of estimating the manganese was employed, we have, I think, fully sufficient causes to account for the failure of Fisher's experiments in arriving at the truth of the case.

§ IV. *Ratio of the Manganese precipitated as Dioxide to the available Chlorine of the higher Chloride.*

A little consideration will at once show that the manganese dioxide contained in the precipitated mixture of oxides (not the *total* manganese precipitated) must bear to the available or loosely combined chlorine of the chloride from which it is precipitated the ratio of 1 : 2 atoms; for, expressed in rather a different way, this amounts to the simple and self-apparent statement that a given quantity of the higher chloride will liberate the same quantity of iodine from potassium iodide, whether it be treated with this latter salt before or after the addition of water (hydrochloric acid being, of course, added in the latter case to dissolve the dioxide precipitated), and though Fisher by proving this to be so (having settled that the whole of the precipitated oxide was dioxide) thought that he could in this way decide the formula of the higher chloride, still in it I can see nothing but the expression of

a fact which could hardly be otherwise than it is. However, in order that no experiment should be omitted which might by any possibilty, however improbable, throw light upon the question under investigation, several determinations were made, the result of which was to verify fully the foregone conclusions.

The method in which these experiments were conducted was precisely similar to that used in determining the ratio of the total manganese precipitated to the available chlorine, detailed in the next paragraph, except that the amount of dioxide contained in the precipitate was determined by the amount of iodine which it would liberate from potassium iodide.

The actual ratios obtained in this way varied between 1 : 2·02 and 1 : 1·982, or, within experimental error, 1 : 2.

§ V. *Ratio of the total Manganese Precipitated to the available Chlorine of the higher Chloride.*

From the fact that the manganese dioxide contained in the mixture of oxides precipitated bears the above ratio to the available chlorine, it follows, as a matter of necessity, that the *total* manganese precipitated must bear to the chlorine a ratio greater than 1 : 2 atoms, since, besides the dioxide, there is also some lower oxide thrown down at the same time. From the various analyses made of the precipitated oxide given in Table I, it follows that this ratio must lie between 1 : 1·524 and 1 : 1·756, and although it was perhaps superfluous to make any direct determinations of this ratio, still, however, a few were made, and these gave the following numbers:—

I.	Ratio found ..	1 : 1·744	IV. Ratio found .. 1 : 1·535
II.	„ „ ..	1 : 1·749	V. „ „ .. 1 : 1·652
III.	„ „ ..	1 : 1·603	VI. „ „ .. 1 : 1·719

all of which lie between the limits assigned above, thus confirming the analyses of the precipitates previously given.

The method in which these determinations were made was as follow:—(1.) A measured portion of the dark solution, obtained by dissolving manganese dioxide in hydrochloric acid, was delivered into a solution of iodide, and the liberated iodine determined by means of a standard solution of sodium thiosulphate; this gave the sum of the free chlorine and loosely combined or available chlorine contained in the liquid. (2.) A second measured volume of the acid solution was poured into 20 volumes of cold water, and the liquid filtered. Since the whole of the higher chloride present is in this way decomposed, the filtrate contains nothing but the uncombined chlorine, and the amount of this latter, after estimation, being deducted from the total

chlorine found in the first operation, gave the quantity of loosely combined chlorine present in a given volume of the liquid; this latter was then compared with the total amount of manganese contained in the precipitate, the analysis being performed as described on p. 659. Fisher, in order to prevent loss of chlorine during the filtration, performed this operation with the aid of an air pump, a **U**-tube with a little solution of potassium iodide being interposed between it and the Woulffe's bottle, in which the funnel was fitted; but although this arrangement would prevent any loss of chlorine from the liquid once it had passed through the filter, it would in no way guard against the loss which must take place while the liquid is in the funnel, while it is being decanted from the vessel in which the dilution with water was effected, and while the acid liquid is actually being diluted; and it was found that unless these three sources of loss were avoided, no satisfactory results could be obtained. The following simple arrangement was therefore adopted:—

The measured portion of the acid solution in which the precipitation was to be effected, was run through a thistle funnel into the requisite quantity of water, contained in a flask through which a current of air was aspirated; this air was then made to pass successively through three vessels containing a solution of potassium iodide, so that the chlorine with which it became laden in the first instance might be entirely absorbed, and subsequently estimated. The stream of air, after having been allowed to continue for three or four hours, was found to have freed the liquid almost entirely from chlorine, so that the precipitate might be filtered off in the air without introducing any source of inaccuracy, and the traces of chlorine still retained in the filtrate estimated, together with the iodine liberated in the absorption flasks and **U**-tube.

In many cases, with the same object in view, a different expedient was adopted. This was simply to free the acid solution of the dioxide from chlorine, before determining the ratio sought. This was found to be especially advantageous, inasmuch as a liquid which is slowly evolving minute bubbles of chlorine, cannot be measured with any great accuracy. It was effected by drawing a very rapid current of air through the manganese solution for a short time. In half an hour the amount of free chlorine present was found to be reduced to about 5 per cent. of its original amount, and after $2\frac{1}{2}$ hours more, only a trace remained in liquid. This rendered it possible to effect the filtration, and also dilution, in the open air, without fear of any estimable loss of chlorine. However long the current of air might be continued, the liquid could never be freed entirely from chlorine, the reason of course being that the higher chloride of manganese present slowly dissociates into the dichloride and free chlorine: but this dissociation

does not proceed with any great rapidity, and an extremely rapid current of air may be drawn through the acid liquid for three days, and at the end of this time the latter will be still quite dark in colour, showing that the whole of the higher chloride has not yet been decomposed. The amount of chlorine carried away by a very rapid current of air from 50 c.c. of the manganese solution after it had been continued for various lengths of time, are given below, together with the amount of higher chloride existing in the liquid at the end of these intervals. The numbers are only approximate.

	Original quantity.	After the current of air had been continued for					
		30 mins.	3 hours.	24 hours.	28 hours.	48 hours.	72 hours.
Grams of chlorine carried off in 5 minutes.....	—	—	0·005	0·002	0·0016	0·0006	0·00028
Higher chloride present	100	86	64	31	—	17	—

In decomposing the solution of the higher chloride in experiments similar to those above described, Fisher substituted a solution of sodium acetate in the place of plain water, in order to prevent the re-solution of the precipitated oxide by the excess of hydrochloric acid present. Experiments, however, failed to detect any such re-solution. The dilute acid liquid, from which a large quantity of oxide had been precipitated, was freed from this precipitate with the exception of a mere trace, which trace was still found in the acid liquid after having been digested with it for over two months; and besides the great improbability that a liquid from which a precipitate is separated, should, without one single factor in the conditions of the experiment being altered, be capable of again taking up that precipitate, still, if such a thing had happened, the results would have been exactly the same as if some of the higher chloride present had escaped decomposition; and since the experiments merely dealt with the ratio of the manganese and chlorine in the *decomposed* portion, it was perfectly immaterial how much of the chloride remained *undecomposed*.

In addition to this, manganous acetate in the presence of free chlorine is decomposed with the formation of manganese dioxide (on which reaction is based a method for the estimation of manganese (Fresenius, *Quat. Anal.*, **1**, 203), and, besides the desirability of introducing no secondary reaction (especially if that reaction be entirely overlooked), a few simple experiments made it at once apparent, that the presence of sodium acetate, so far from making the precipitation more complete, only retarded and hindered it. This retardation, of course,

became more and more marked as the strength of the sodium acetate solution was increased, so that with a 15 per cent. solution, the quantity of higher chloride decomposed after two hours did not amount to half that decomposed immediately when an equal volume of water was used instead of the acetate; and even after a space of three days the liquid still remained quite dark, and was found to contain 20 per cent. of the chloride still undecomposed, although the amount of the precipitate formed showed that some of the manganous acetate present had suffered decomposition, the free chlorine having entirely disappeared. The same phenomena were observed, though to a proportionately smaller extent, with 10 and 5 per cent. solutions of the acetate. However, as is seen in Table I, it happened that the use of the acetate could not have introduced any appreciable error into either the composition of the precipitate, or the determination of the ratio; the reasons given on p. 661, perhaps with some loss of free chlorine as pointed out on p. 663, being amply sufficient to account for Fisher having obtained a ratio of somewhat over 2 : 1, in place of about 1·64 : 1.

§ VI. *Secondary Reactions considered.*

The question as to whether the composition of the various precipitates obtained could be attributed to any secondary reactions, was now attacked and decided in the negative. The secondary actions which might possibly take place are:—

1. That the dioxide, or an oxide richer in oxygen than the precipitates obtained, being thrown down in the first instance, it is subsequently attacked by the hydrochloric acid present in such a manner as to reduce some of it to protoxide (sesquioxide, see p. 657). This would entail the formation of some free chlorine, or the reformation of some of the higher chloride. But the acid liquid having been freed from free chlorine before decomposition, it was found that neither of these bodies were present after decomposition, thus proving that no such secondary reaction could have taken place.

2. That the sesquioxide, or an oxide poorer in oxygen than the precipitates obtained, being thrown down in the first instance, it is subsequently attacked by the free chlorine, or by the hydrochloric acid present, in such a manner that it is rendered richer in dioxide.

That the chlorine present does not act in such a manner, is seen from the fact that its presence has no effect on the composition of the precipitates obtained (see analyses 3, 7, 14, and 15, Table I); and that the hydrochloric acid does not act in such a manner, was proved by digesting a precipitate obtained with acid sufficiently strong to dissolve it slowly, in which way it was found that the action of the acid tended to diminish, instead of increasing the relative propor-

tion of the dioxide present (though even this reaction under the circumstances of the precipitation cannot take place to any appreciable extent, as shown above). The results obtained were as follows:—

	Mn as MnO	:	Mn as MnO_2
After precipitation	1	:	6·204
After digestion with acid of strength 1 : 7 ..	1	:	4·376
„ „ „ 1 : 4 ..	1	:	2·500

Seeing, then, that all possible secondary reactions are incapable of explaining the peculiar and variable composition of the substance precipitated, we must conclude that a mixture of oxides, and not a definite oxide, is precipitated in the first instance, and that this mixture is not subsequently altered in composition. Hence, assuming for the present that the higher chloride is Mn_2Cl_6, its decomposition by water will be represented by the following equations:—

$$\text{I. } x[Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl],$$
$$\text{II. } y[Mn_2Cl_6 + 3H_2O = Mn_2O_3 + 6HCl],$$

taking place simultaneously, but in various proportions, the average values for x and y obtained being about 4 and 1 respectively.

§ VII. *Action with dilute Acids.*

A series of experiments was made, using acids of different strength, in order to examine the influence exerted by the presence of water on the stability of the higher chloride. The amount of this body present on any occasion was estimated by pouring the solution of it into an excess of water and ascertaining the amount of manganese *dioxide* contained in the precipitate, this affording a true measure of the higher chloride from which it is obtained, since it always bears to it a constant ratio (p. 661).

The mode of performing the experiments in this series, as well as those in the series to be hereafter described, was as follows:—A weighed quantity of the dry dioxide (p. 656) was transferred to a short wide test-tube (3 inches in length by 1 inch in diameter), a measured quantity of water was then added, and subsequently a measured volume of acid, the tube with its contents being immersed in a water-bath kept at a constant temperature. The action was, in this series of experiments, allowed to continue for 15 minutes, during the 1st, 6th, and 11th minute of which the contents of the tube were vigorously stirred with a glass rod. After the 15 minutes had elapsed the acid liquid was poured into 20 volumes of cold water, from which the precipitated oxides were subsequently separated by filtration, and the amount of dioxide present determined volumetrically. In order

to obtain results in any way consistent or comparable with each other, strict attention to every particular above mentioned was found to be absolutely necessary. A mean of the results obtained is given in Table II, in which column 1 gives the proportion of acid to dioxide taken; column 2, the density of the aqueous acid used; column 3, the proportions of water and anhydrous HCl present after the solution was complete; and column 4, the amount of dioxide precipitated on dilution, that originally taken being 100; this column therefore represents the relative amount of the higher chloride formed under the various conditions mentioned.

TABLE II.—*Showing the effect of Water on the Stability of the Chloride.*

1. Proportion of HCl to MnO_2 taken; in molecules.	2. Density of acid used, 15° C.	3. Molecules of water present to every 10 of HCl after solution.	4. Relative amount of manganese converted into Mn_2Cl_6.
1. 50 : 1	1·1958	41·65	43·69
2. 50 : 1	1·1891	44·24	40·31
3. 50 : 1	1·1816	47·05	38·62
4. 50 : 1	1·1768	49·73	37·61
5. 50 : 1	1·1651	52·58	36·71
6. 50 : 1	1·1580	57·73	34·79

This table clearly shows that less of the higher chloride is formed according as the proportion of water present is greater. When represented diagrammatically it furnishes a curve which is rather sudden from experiments 1 to 2, less so from 2 to 3, while from 3 to 6 it does not differ much from a straight line. On repeating the different experiments with all due precautions a maximum variation of about 1 per cent. was observed, which would make no material alteration in the nature of the curve, although it showed that no great degree of accuracy could be expected.

Since it was impossible to increase the relative amount of water present, and at the same time to keep the actual amount of acid the same without increasing the bulk of the liquid, it seemed to be possible that the decrease in the amount of the higher chloride present might not be due to the direct action of the water, but merely to the increased volume of liquid present, which would favour dissociation. In order, if possible, to decide upon this point another series of experiments was performed, each one being performed under precisely similar circumstances to those in the above series, except that the quantity of liquid present was kept constant, this, of course, necessitating that the proportion of acid to manganese dioxide taken, should

be altered slightly in each case, but, inasmuch as a very large excess of acid was always present, this would probably introduce no appreciable error. The results of these experiments confirmed the above-mentioned supposition, and showed that the presence of small quantities of water did not diminish the amount of the higher chloride formed, its only influence on the reaction being to cause the solution of the dioxide taken to be effected less rapidly.

The decomposition of the chloride by a very large excess of water has already been sufficiently discussed.

§ VIII. *Influence of the Amount of Acid employed.*

A few experiments were next made, in which the actual quantity of hydrochloric acid used was increased without increasing its amount relative to the water present; this was effected by dissolving weighed quantities of the dioxide in various proportions of the aqueous acid. The actual proportions used were 1 mol. of the dioxide to 12, 25, 50, 100, 200, 300, and 400 mols. of the acid. In the first series of experiments the time allowed for the solution was two minutes, and this series showed a steady, though not large *decrease* in the amount of the higher chloride formed, in proportion as the quantity of acid was increased. In the second series of experiments the time allowed for solution was 15 minutes, and here the amount of higher chloride was found to be *increased* by increasing the quantity of acid, the increase being much more marked in the first three experiments than in the last four. The only explanation which I can offer of these anomalous results is the following:—The dissociation products of the higher chloride are manganous chloride and nascent chlorine. Any circumstance tending to remove either of these bodies from the sphere of action, would diminish the amount of the higher chloride present at any given moment, thus a small diminution in the bulk of the acid employed, would probably increase the amount of higher chloride present, by the dissociation products being dispersed through a smaller space; this is illustrated by the experiments given in Table II; but when there is a very great diminution in the bulk of the liquid employed the greater proportion of the chlorine liberated, would not be retained in the liquid, but would be evolved, and thus removed from the sphere of action, diminishing the quantity of the higher chloride present. The amount of dissociation thus effected would become more apparent as the time allowed was longer, and thus the second series of experiments might yield results contradictory to those yielded in the first series, which were the more correct in showing what was sought, inasmuch as the secondary effects due to the diminution in the amount of acid used, could not take place to such a large extent.

A striking illustration of the injurious effect of an increased proportion of acid on the higher chloride, was accidentally afforded in the series of experiments to be next described.

There, therefore, seems to be no ground for Fisher's twice repeated statement "that a large excess of hydrochloric acid is found to render manganese tetrachloride comparatively more stable," and still less for the conjecture "that this body probably exists only in combination in a form analogous to chloroplatinic acid."

§ IX. *Solution of the Dioxide in presence of Manganese Dichloride.*

Having studied the reaction so far, experiments were next made with a view of deciding whether the higher chloride formed was in reality $MnCl_4$, or whether it was Mn_2Cl_6, or any other chloride agreeing with the general formula Mn_nCl_{2n+2}.

The following method of attacking this question suggested itself. If the chloride formed is $MnCl_4$ then it can make no difference to the amount of this chloride obtained, whether the solution be performed in pure acid, or in acid containing a quantity of manganese dichloride; whereas, if the body be Mn_2Cl_6, then, by performing the solution of the dioxide in the presence of a sufficient quantity of manganous chloride we might succeed in converting the whole of the oxide, together with some of the dichloride, into the higher chloride, so that, on decomposing it with water, we should get as much dioxide precipitated as we dissolved. Thus:—

$$\text{I. } MnO_2 + 4HCl + MnCl_2 = Mn_2Cl_6 + 2H_2O.$$

and then on decomposition—

$$\text{II. } Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl,$$

otherwise, if no dichloride were added to the acid, we should not be able to obtain in the precipitate more than half, at the most, of the dioxide dissolved. Thus:—

$$\text{III. } 2MnO_2 + 8HCl = Mn_2Cl_6 + 4H_2O + Cl_2.$$
$$\text{IV. } Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.*$$

Consequently, a series of experiments was made, in which a given weight of the dioxide was taken, and dissolved in a definite quantity of acid (50 mols. of HCl) in the presence of varied proportions of the dichloride; but, since this salt is not easily soluble in strong acid, it was added in the form of a concentrated solution (containing 55 per cent. $MnCl_2$) before the addition of the acid, the experiments being performed similarly to those given in Table II, only two minutes,

* In these equations the manganese precipitated as protoxide is left out of consideration, as it does not in any way affect the argument.

however, being allowed for the solution. The results thus obtained are represented in the form of a curve in Plate I, in which the abscissæ represent the molecules of $MnCl_2$ added for every 1 mol. of MnO_2, and the ordinates represent the amount of dioxide precipitated, the dioxide taken being 100.

This curve shows that the amount of the higher chloride obtained from a given quantity of the dioxide is very greatly increased by the presence of some manganese dichloride; but it shows even more than this, namely that this higher chloride which is formed in the reaction is Mn_2Cl_6; for the curve, which, up to the addition of a whole molecule of $MnCl_2$, differs but little from a straight line, at once, after this quantity has been added, changes its nature altogether, showing that at this point, some factor in the reaction has been changed, or some condition has been satisfied, which condition, I think, can only be that which allows the Equation I, p. 669, to be realised. The reason why a maximum in the amount of the higher chloride formed is not at once attained at the point E is of course obvious, namely, that when only exactly sufficient constituents are present to form 100 parts of the sesquichloride, the dissociation of this latter unstable body is very much greater than when an excess of one of these constituents is present, as at F, G, H, &c. The portions of two other curves shown in the diagram, namely, K, L, M, and N, O were obtained in the first series of experiments made, in which, after G, the proportion of acid used was increased to one and a-half times its original amount, and after M to twice its original amount. The modifications thus introduced cannot possibly be accounted for simply by the increased volume of the liquid present: for at K, although there is a considerably larger relative as well as actual proportion of manganese dichloride present than at E, still there is less of the higher chloride formed, and similarly at N there is less formed than at K, L, E, &c. The only possible explanation is that an excess of acid is prejudicial to the stability of the higher chloride. The slight relative increase in the bulk of liquid used, owing to the addition of successively increasing volumes of the dichloride solution, would, no doubt, introduce some modification into the main curve, but it could scarcely influence its general nature, and would only tend to make that which it should illustrate, less apparent, by relatively lowering the upper portion, G, H, I, J.

§ X. *Influence of Temperature.*

Attempts were made to obtain the same sort of evidence as that obtained in the previous paragraph, but in a different manner. The following argument appeared to promise some success:—

Seeing that a rise of temperature materially decreases the stability of the higher chloride, while a reduction of temperature increases its

Plate I.

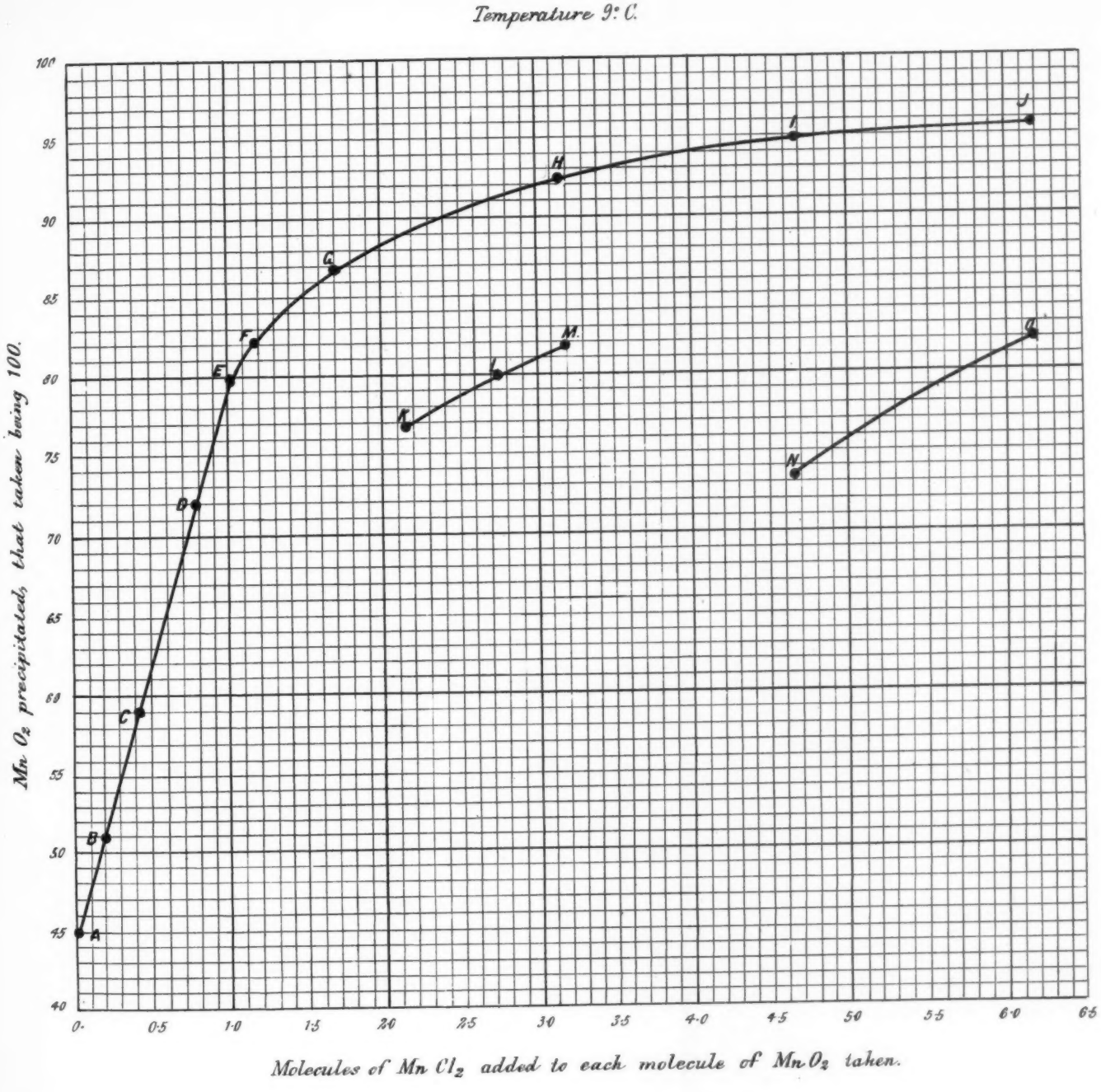

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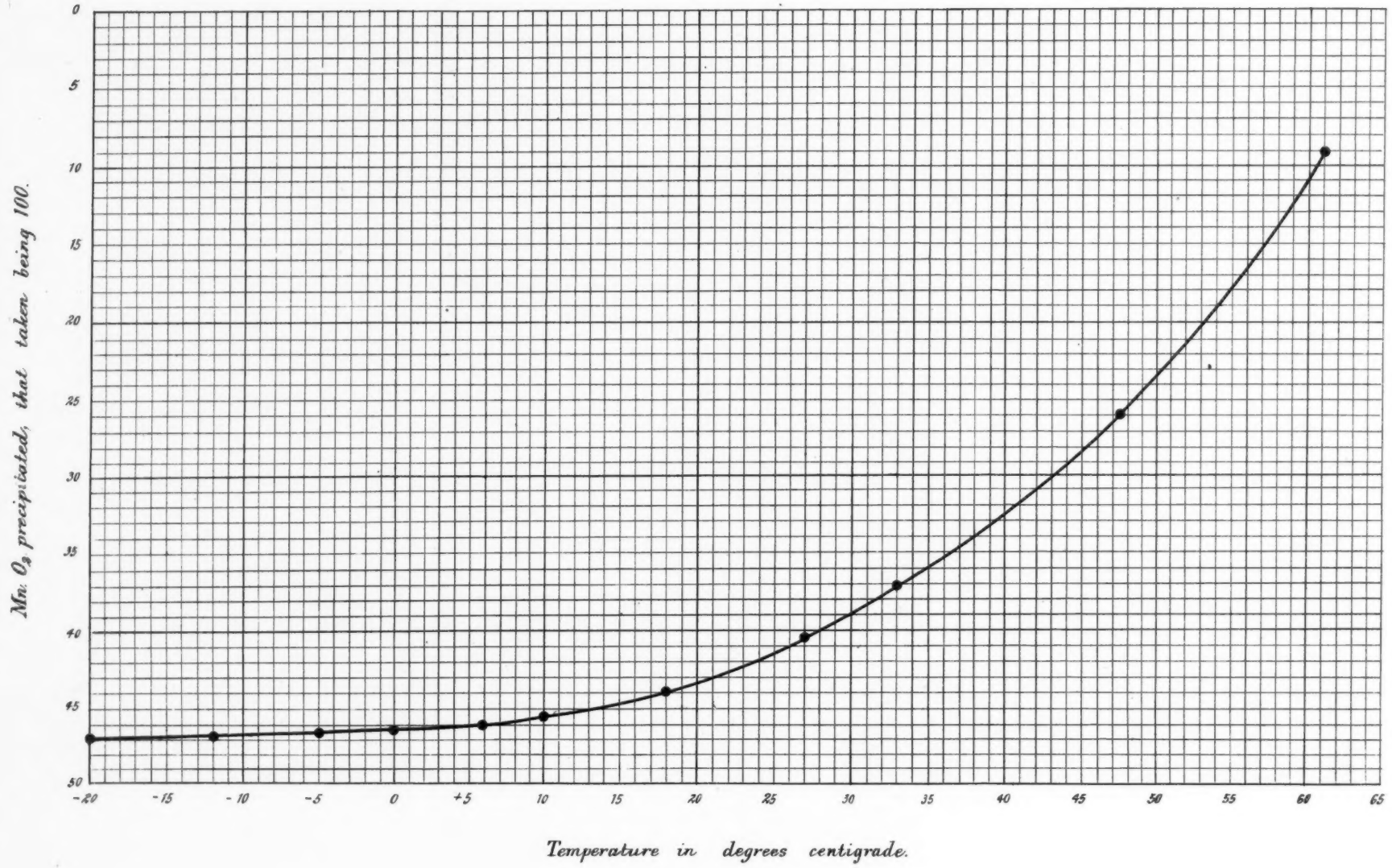
Plate 2



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stability, then by performing the solution of the dioxide at a sufficiently low temperature, there could be no reason why more than 50 per cent. of it should not be converted into the higher chloride, if this higher chloride is $MnCl_4$, according to the equation—

$$\text{I. } MnO_2 + 4HCl = MnCl_4 + 2H_2O,$$

in which it is seen that as much as 100 per cent. of the manganese used may be converted into the tetrachloride, and subsequently precipitated entirely as dioxide, thus:—

$$\text{II. } MnCl_4 + 2H_2O = MnO_2 + 4HCl,$$

whereas, if the higher chloride formed were Mn_2Cl_6, by no possibility could more than 50 per cent. of the manganese used, be obtained in the precipitate as dioxide, on decomposing the liquid with water, as is shown by the following equations:—

$$\text{III. } 2MnO_2 + 8HCl = Mn_2Cl_6 + Cl_2 + 4H_2O.$$
$$\text{IV. } Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl.$$

A series of experiments was therefore performed, precisely similar in every respect, except that the temperature was varied. The results obtained are given in the form of a curve, Plate II, where the abscissæ are the temperatures, and the ordinates the amount of dioxide precipitated, the dioxide taken being 100.

This curve shows that when the solution of the dioxide is performed at a temperature of 60° C., less than 10 per cent. is reprecipitated on decomposing the solution with water, and that as the temperature is lowered, the amount thus precipitated becomes rapidly greater, till at 10° C. it amounts to 45 per cent. of the dioxide taken, and this amount is not increased as much as 2 per cent. by subsequent fall of 30° C.; we cannot obtain more than 50 per cent. of the dioxide taken in the precipitate, or, in other words, we can never realise the reaction represented in Equations I and II, but only those represented in III and IV: that is, the higher chloride is Mn_2Cl_6, and not $MnCl_4$.

These experiments, as well as those detailed in the last paragraph, also prove conclusively that the higher chloride is not Mn_3Cl_8, or any chloride corresponding to the general formula Mn_nCl_{2n+2}, in which n has a value greater than 2; for, in the one case, if the chloride were Mn_3Cl_8, we should not be able to get more than one-third instead of one-half of the manganese dioxide reprecipitated; and in the other, the addition of 1 mol. of the dichloride could not possibly have caused as much as 80 per cent. of this oxide to have been thrown down.

§ XI. *Attempts to obtain a Double Salt of the Sesquichloride.*

Seeing that nearly all chlorides on which the experiments have been tried have yielded a double salt of some description or other, attempts

were made to obtain a double salt of manganese sesquichloride with ammonium chloride. For this purpose some of the dioxide was dissolved in hydrochloric acid, in the presence of an excess of ammonium chloride. The dark solution thus obtained, after being filtered through spun glass, was found to become more quickly colourless than a similar solution containing no ammonium chloride. On being allowed to evaporate spontaneously, very hard brown crystals in the form of cubes were obtained, which, on being recrystallised from water, were found to be a double salt of manganese dichloride, and not of the sesquichloride; they corresponded perfectly to the formula, $MnCl_2,2NH_4Cl,H_2O$.*

Sodium chloride and potassium chloride appear to act similarly to ammonium chloride, aiding the decomposition of the sesquichloride, and forming probably some double chloride with manganous chloride, although the bodies thus obtained were not analysed. Here, again, we find no grounds for Fisher's statement that the presence of alkaline chlorides increases the stability of the higher chloride of manganese.

§ XII. *Nicklès' Experiments.*

Nicklès (*Ann. Chim. Phys.* [4], **5**, 161), by passing a current of dry gaseous hydrochloric acid into ether in which manganese dioxide was suspended, obtained a green liquid, the analysis of which on one occasion corresponded tolerably well with the formula, $MnCl_4,12C_4H_{10}O,2H_2O$. This, however, can scarcely afford any evidence for the existence of manganese tetrachloride, inasmuch as the analytical numbers obtained would answer equally well to the formula, $Mn_2Cl_6,24C_4H_{10}O,2HCl,4H_2O$; and even if this were not the case, much weight could hardly be attached to the analysis of unstable liquids, which, although the experiment was repeated a great number of times, could never be obtained twice answering to the same formula, but which "*variaient singulièrement par leur composition.*"

§ XIII. *Summary.*

In conclusion it may be well to sum up briefly the main points proved in this paper.

1. When a solution of manganese dioxide in strong hydrochloric acid is diluted with water, a mixture of oxides is precipitated, which is indefinite in composition, and may generally be represented by formulæ intermediate between $16MnO_2$, $5MnO$, and $36MnO_2$, $5MnO$.

2. The manganese contained in this precipitate as dioxide bears to

* According to v. Hauer, these crystals contain 2 molecules of water, but according to Rammelsberg only one: the present experiments, therefore, confirm the statement of the latter chemist.

the loosely combined chlorine of the higher chloride from which it is precipitated, the ratio of 1 : 2 atoms.

3. The total manganese precipitated, therefore, bears to this chlorine the ratio of about 1 : 1·64 atoms.

4. When the solution of the dioxide is performed in weaker acids, the amount of the higher chloride formed is not appreciably diminished.

5. An increase in the actual amount of the aqueous acid employed for the solution, is prejudicial to the stability of the higher chloride formed.

6. The higher chloride formed in this reaction is Mn_2Cl_6, and not $MnCl_4$, the solution of the dioxide and sesquioxide by hydrochloric acid, and the subsequent decomposition of the sesquichloride formed, being represented by the following equations:—

$$\text{I.}\quad Mn_2O_3 + 6HCl = Mn_2Cl_6 + 3H_2O,$$

$$\text{II.}\quad 2MnO_2 + 8HCl = Mn_2Cl_6 + Cl_2 + 4H_2O,$$

$$\text{III.}\quad \begin{cases} x[Mn_2Cl_6 + 2H_2O = MnO_2 + MnCl_2 + 4HCl], \\ y[Mn_2Cl_6 + 3H_2O = Mn_2O_3 + 6HCl], \end{cases}$$

in which the average values for x and y are 4 and 1 respectively.

LXVII.—*On the Decomposition of the Simple Weight χ effected by Victor Meyer.*

By Sir B. C. Brodie, Bart., F.R.S.

It will not, I trust, be considered inappropriate to the occasion if I offer to the Chemical Society a few remarks on the relation of the views which I have propounded in my two memoirs* on the "Calculus of Chemical Operations" upon the nature of certain chemical elements to the important discoveries of Victor Meyer.

In that calculus the letter α is the symbol of the operation performed upon the unit of space, of which the result is a unit of hydrogen. The weight of this unit is assumed as the unit of comparison, and has assigned to it the weight 1. This relation is expressed in the equation $w(\alpha) = 1$. The letter χ is the symbol of that operation, the result of which performed upon the unit of hydrogen is

* *Phil. Trans. Roy. Soc.*, Part II, 1866, p. 781, and Part I, 1877, p. 35; *Chem. Soc. J.*, **21**, p. 367. *Moniteur Scientifique*, Quesneville, Mars, 1879. Tome ix, p. 243; traduit par le Dr. A. Naquet.

a unit of hydrochloric acid which is symbolized indifferently as $\chi\alpha$ or $\alpha\chi$, since $w(\alpha\chi) = 18{\cdot}25$, $w(\chi) = 17{\cdot}25$.* A unit of chlorine is the result of the repetition of this operation. The symbol of that unit being $\alpha\chi^2$, so that $w(\alpha\chi^2) = 35{\cdot}5$. These symbols, χ and α, are therefore primarily and essentially symbols of operations of the nature of which we are ignorant and which are known to us by their result alone, and any further assumption as to their nature is of a character more or less speculative.

The symbol of the unit of chlorine is one of a numerous class. The same order of considerations which leads to the symbol $\alpha\chi^2$ for chlorine leads to the symbols $\alpha\omega^2$, $\alpha\beta^2$, $\alpha\nu^2$, $\alpha^2\phi^4$ . . . as the symbols of iodine, bromine, nitrogen, phosphorus, and generally the symbols of those elements which are termed elements of uneven atomicity are similar in form to these.† There are also certain symbols of compound substances which belong to the same category, among which I may specially mention the binoxide of hydrogen, $\alpha\xi^2$.

The simple weights, α, χ, ω, β, ν, ϕ, ξ, . . . are in the strictest sense, according to the definitions, simple or undistributed weights, or at least have hitherto been correctly so regarded, for there has been no evidence of the "distribution"‡ of these simple weights, that is, of the resolution of these weights into their components in that total system of chemical phenomena which is the field of chemical study. There are, however, other chemical symbols of the same form, such as for example the symbol of the unit of binoxide of chlorine, $\alpha(\chi\xi)^2$, and of methyl, $\alpha(\kappa\alpha)^2$, in the case of which the portions of matter, $\chi\xi$, $\kappa\alpha$, appear to us, even through extensive systems of events, as simple or undistributed weights, but do not retain this character throughout the total system of chemical phenomena, being in the total system resolved into their components.§

* Ref. Part I, Sec. V. † Part I, Sec. VII, 5, 6, 7, 8, 9, 10.

‡ Conf. Part I, Sec. I, Def. 7, 8, 10, 11, 12.

§ The terms "simple," and "undistributed" weights are relative terms, and do not, like the term "atom," imply any theory as to the indivisibility of matter. The following are the definitions I have given of these terms, Part I, Sec. I (12):—

"The term 'distribution of weight' may be defined as that operation by which a compound weight is resolved into its component weights, or by which it is made up from those weights, regard being had to some special system of such events which is the subject of consideration.

"A 'distributed weight' is a weight which, in such a system of events, is resolved into two or more weights, or made up from such weights.

"An 'undistributed weight' is a weight which, in the same system of events, is not so resolved or so made up. An undistributed weight may also be defined as a weight which is resolved into one weight, or made up from one weight alone.

"The division of weights into distributed and undistributed weights is co-extensive with the previous division of the same into compound and simple weights."

The inference derived from these symbols is of an important character, for if we admit (1) that the units of these elements are thus constructed, and also (2) that the units of all other chemical substances with which we are acquainted may be resolved into some number of units of these elements, together with some number of units of the other group of elements with the symbols assigned to them in my memoir, that is to say, of the form π^n, the great chemical generalization discovered by Laurent and Gerhardt, as an empirical law, the law of even numbers,* follows as a necessary consequence of these principles, and may be deduced from them.

Now it is not possible positively to assert from these symbolical expressions that the units of these elements are capable of being actually decomposed into the unit of hydrogen, and the units symbolized as $\chi, \beta, \omega, \nu, \phi \ldots$ in the way of which resolution impediments of an order unknown to us may be placed, nor is this necessarily even implied in those symbols. "So far as the principles or conclusions of this method are concerned" (as I have elsewhere said), "the simple weights $\xi, \theta, \chi, \beta, \omega, \nu, \phi \ldots$ may be treated purely as 'ideal' existences, created and called into being to satisfy the demands of the intellect, to enable us to reason and to think in reference to chemical phenomena, but destined to vanish from the scene when their purpose has been served, and the existence of which as external realities we neither assume nor deny." But, nevertheless, a real interpretation is unavoidably suggested to us by the symbols, and we cannot but surmise that the "simple weights" which appear to us now as "implicit and dependent existences," may some day become or may in the past have been "isolated and independent existences.†" And besides, there are various arguments from which such a real interpretation is rendered probable.

Among the arguments in support of this view is one which I have discussed at some length in my second memoir, namely, the case of the binoxide and tetroxide of nitrogen. From the peculiar densities of the gases called by these names, there is great reason to believe that chemists have long had in their hands, without recognising the fact, the products of the decomposition of the element nitrogen. The densities of the binoxide and tetroxide of nitrogen are said to be "abnormal," but it would be more correct to say that the densities of certain gases which chemists have assumed, without adequate reason, to be the densities of the binoxide and tetroxide of nitrogen, do not concur with this assumption. There is no improbability in the belief that in respect of this assumption chemists may have been mistaken, and that the assumption is erroneous; indeed,

* Conf. Part II, Introduction, "On the Law of Even Numbers," pp. 49, 52.

† Part I, Conclusion, p. 859.

in numerous cases presenting similar features, which have been adequately investigated, it has been demonstrated that the cause of the so-called abnormal vapour-density has been the decomposition of the chemical substance of which the density is abnormal; but it is eminently improbable that an exception should exist to the most general and well established law of chemistry.

The researches of Victor Meyer have demonstrated that the density of the element chlorine itself presents in these respects an exact parallel to the densities of the binoxide and tetroxide of nitrogen, and exhibits the same peculiarity.

In the course of a series of exact investigations on the gaseous densities of chemical substances at elevated temperatures, Victor Meyer took the density of chlorine gas at temperatures ranging (according to his estimate) from 600° to 1,567° C., with the result shown in the following table (*Deut. Chem. Ges. Ber.*, **12**, 1426):—

Table of Density of Chlorine Gas. Density of Air = 1.

Temperature.	Density (2 experiments).	
620°	2·42	2·46
808	2·21	2·19
1,028	1·85	1·89
1,242	1·65	1·66
1,392	1·66	1·67
1,567	1·60	1·67

The density of chlorine as calculated from the symbol $\alpha\chi^2$ is 2·45; two-thirds of this number is 1·63. It may therefore, from these experiments, be asserted that chlorine gas at a temperature of 1,242° C. is resolved into certain other substances, the aggregate density of which is two-thirds the density of chlorine, and does not change between the temperatures 1,242° and 1,567° C.

By the side of these facts let me now place the experimental determinations of the density of the tetroxide of nitrogen. The results given in the following table above the temperature of 20° C. are due to Deville and Troost; at and below that temperature to Müller and to Playfair and Wanklyn.*

* *Proc. Roy. Soc. Edin.*, **4**, 395; *Compt. rend.*, **64**, 240; *Dict. de Chim.*, 1, 490.

Table of the Density of Tetroxide of Nitrogen. Density of Air = 1.

Temperature.	Density.	Temperature.	Density.
4·2°	2·59	70·0°	1·02
11·3	2·64	80·6	1·80
24·5	2·52	90·0	1·72
20·0	2·70	100·1	1·68
26·7	2·65	111·3	1·65
35·4	2·53	121·5	1·62
39·8	2·46	135·0	1·60
49·6	2·27	154·0	1·58
60·2	2·08	183·2	1·57

It appears from these observations that the density of the gas assumed to be the tetroxide of nitrogen varies according to the temperature at which that density is taken, from about 2·6° between the temperatures 4·2° and 26·7° C., to about 1·6° C. between the temperatures of about 111·3° and 183·2° C., the density gradually passing between 26·7° and 111·3° C. from one of these limits to the other. The density assigned by theory to the tetroxide of nitrogen, $\alpha\nu^2\xi^4$, is 3·19. The tetroxide of nitrogen, therefore, with its true theoretical density, has not been discovered. $\frac{4}{5} \times 3{\cdot}19 = 2{\cdot}55$, which closely approximates to the density between the temperatures 4·2° and 35·4° C. $\frac{1}{2} \times 3{\cdot}19 = 1{\cdot}59$, which closely approximates to the density of the gas between 100° and 183 C°. These facts present the strictest similarity to the changes observed by Victor Meyer in the density of chlorine. Similar observations apply to the binoxide of nitrogen, of which the theoretical density corresponding to the symbol $\alpha\nu^2\xi^2$ is 2·09, the number actually found by experiment for this density 1·04 being one-half the theoretical density.*

The symbols of the units of the gases corresponding to these densities cannot be expressed by any integral number of the prime factors, α, ν, ξ, but are in the two cases respectively—

Binoxide of nitrogen, $\alpha^1\nu\xi$
Tetroxide of nitrogen, $\alpha^1\nu\xi^2$.

These apparent anomalies may be explained by the assumption that the binoxide and tetroxide of nitrogen do not exist in the gaseous condition, but are respectively resolved, at the temperatures at which their density has been assumed to be taken, into two other gases. The result of this would be to diminish by one half the apparent density of the gases in question. Such an explanation would doubtless have long since been applied to the case, but on the prevailing theory of the

* Conf. Part I, Sec. VIII (2).

constitution of these substances, the explanation is inapplicable. The case is otherwise on the view I have given. In Part II I have thrown out a suggestion in illustration of the kind of decomposition of these gases, by which these anomalies would be explained, which is given in the following equations:—

$$1 + \alpha\nu^2\xi^2 = \alpha\nu\xi + \nu\xi$$
$$1 + \alpha\nu^2\xi^4 = \alpha\nu\xi^2 + \nu\xi^2.$$

For the further discussion of this question I must refer the reader to Part I, Sec. VIII (2), and II, p. 61.

Now if we apply similar principles to the case of chlorine, the most obvious hypothesis we can frame as to the decomposition of chlorine in V. Meyer's experiment is given in the equation—

$$1 + 2\alpha\chi^2 = 2\alpha\chi + \chi^2,$$

which assumes two units of chlorine to be decomposed into two units of hydrochloric acid, and a unit symbolized as χ^2 where $w(\chi^2) = 34{\cdot}5$. The decomposition here expressed would be exactly analogous to the decomposition of binoxide of hydrogen into water and oxygen, according to the equation—

$$1 + 2\alpha\xi^2 = 2\alpha\xi + \xi^2$$

The equation—

$$2\alpha\chi = \alpha + \alpha\chi^2$$

being represented by the equation—

$$2\alpha\xi = \alpha + \alpha\xi^2$$

and the equation—

$$1 + \alpha\chi^2 = \alpha + \chi^2$$

being represented by the equation—

$$1 + \alpha\xi^2 = \alpha + \xi^2$$

in which equations the units χ^2, $\alpha\chi$, $\alpha\chi^2$, correspond to the units ξ^2, $\alpha\xi$, $\alpha\xi^2$. The decomposition of chlorine according to the equation—

$$1 + 2\alpha\chi^2 = 2\alpha\chi + \chi^2,$$

would be attended with the change of density observed by Meyer, and on this hypothesis the discovery of Meyer would consist in the discovery of a new element, χ^2, analogous to oxygen, of which we might speak as the "oxygen of hydrochloric acid."*

* H. Kopp in his memoir on specific heats, observes that the peroxide of hydrogen, "HO," has in its solid combinations nearly the same atomic heat as iodine, bromine, and chlorine, the atomic heat of "HO" being, according to his views, $2{\cdot}3 + 4 = 6{\cdot}3$, and the atomic heat of these elements I, Br, Cl, 6·6. This would also be the case, he continues, for the analogous peroxides of unknown elements of the same atomic

But the researches of V. Meyer have rendered it eminently probable (we cannot perhaps as yet say certain) that oxygen itself is a product of the decomposition of chlorine. The evidence on which this important statement is based is as follows :—Chlorine generated in the usual manner was passed through an elaborate desiccating apparatus, including tubes containing phosphoric anhydride nearly two metres in length, and was thence passed through a thin platinum tube into the porcelain bulb (or retort), which V. Meyer uses for the determination of vapour-densities, and thence by a gas delivery tube through a solution of hydrate of soda. The bulb was heated to 600° C., and chlorine passed through it for four hours. The temperature was then raised to 1200—1500° C., and at once a gas appeared which was not absorbed by the solution of soda, and which turned out to be pure oxygen.

The apparatus for generating and purifying chlorine being very complicated, Victor Meyer employed another and simpler method for procuring the gas, namely, by the decomposition of protochloride of platinum. This compound can be easily made absolutely pure and dry. It is not hygroscopical, and yields chlorine by the application of moderate heat in a tube of hard glass. From such a tube the gas was directly led into the porcelain bulb, the experiment otherwise being conducted as before. The result obtained was the same as in the former experiment.

The results of the experiment as regards the oxygen produced, are precisely the same when in place of a solution of soda a solution of iodide of potassium, or even metallic mercury, is employed for absorbing the chlorine. Several experiments were made in this last form. The proportion of oxygen collected is very small, from $\frac{1}{2}$ to 1 per cent. of the chlorine passed through the apparatus. But yet considering the great precautions taken in these experiments, we can hardly escape the conclusion that this oxygen had its origin in the decomposition of chlorine. If so, we are compelled to assume the simple weight χ itself to have been decomposed, so that $\chi = \chi'\xi$, χ' and ξ being the two constituents of χ. Since $w(\chi'\xi) = 17{\cdot}25$, $w(\chi') = 9{\cdot}25$. The result of the decomposition is expressed in the equation—

$$1 + 2\alpha\chi'^2\xi^2 = 2\alpha\chi'^2\xi + \xi^2$$

heat as hydrogen. The specific heat, therefore, of chlorine agrees with the hypothesis of its being such a peroxide, although it affords no evidence that it actually is so.

These remarks equally apply to the hypothesis here given as to the constitution of chlorine, namely, that chlorine is constituted of hydrogen, and the unknown element χ^2 analogous to oxygen. In this case we have

$$\text{Sp. h. } (a) \times w(a) + 2 \text{ Sp. h. } (\chi) \times w(\chi) = 6{\cdot}6,$$

which gives sp. h. $(\chi) \times 17{\cdot}5 = 2{\cdot}15$, being half the atomic heat assigned by H. Kopp to solid oxygen.—*Annalen der Chemie*, Suppl. Band III, S. 338.

which corresponds to the observed change of density. On this assumption the unit of chlorine is constituted of a unit of the hypothetical element $\alpha\chi'^2$ (murium), and of a unit of oxygen ξ^2, and in this decomposition two units of chlorine are resolved into two units of the oxide of that element and a unit of oxygen. Hence we have for the symbols of the units of matter participating in these changes—

	Symbol.
Chlorine.....	$\alpha\chi'^2\xi^2$
Hydrochloric acid.....	$\alpha\chi'\xi$
,, ...	$\alpha\chi'^2\xi$
,, ...	$\alpha\chi'^2$

the result of the decomposition of hydrochloric acid into hydrogen and chlorine being on this view to be thus expressed:—

$$2\alpha\chi'\xi = \alpha + \alpha\chi'^2\xi^2$$

where $w(\chi') = 9{\cdot}25$, $w(\alpha\chi'^2\xi) = 27{\cdot}5$, and $w(\alpha\chi'^2) = 19{\cdot}5$.

We may remark that this last weight closely approximates to half the assumed density of the hypothetical element fluorine, which is 38.

Now the units $\alpha\chi'^2\xi$ and $\alpha\chi'\xi$ are related to one another precisely as are the units of the oxide of chlorine $\alpha\chi^2\xi$, and of hypochlorous acid $\alpha\chi\xi$, and it might be anticipated that when the unit $\alpha\chi'^2\xi$ was brought in contact with water, hydrochloric acid would be formed according to the equation—

$$\alpha\chi'^2\xi + \alpha\xi = 2\alpha\chi'\xi.$$

Hence the only substances which would be found on leading the gases arising from the decomposition of chlorine into water would be hydrochloric acid and oxygen, the result being attained in the following stages:—

$$1 + 2\alpha\chi'^2\xi^2 = 2\alpha\chi'^2\xi + \xi^2$$
$$2[\alpha\chi'^2\xi + \alpha\xi = 2\alpha\chi'\xi],$$

the total result being—

$$1 + 2\alpha\chi'^2\xi^2 + 2\alpha\xi = 4\alpha\chi'^2\xi + \xi^2,$$

which is precisely the same result as that attained in the immediate decomposition of water by chlorine, with the formation of oxygen and hydrochloric acid, from which it could not be discriminated.

We should expect this same result to be also attained if the chlorine were decomposed according to the equation—

$$1 + 2\alpha\chi^2 = 2\alpha\chi + \chi^2,$$

for the unit χ^2 might be expected to decompose water with formation of hydrochloric acid and oxygen according to the equation—

$$\chi^2 + 2\alpha\xi = 2\alpha\chi + \xi^2,$$

the final result being given in the algebraical sum of these equations—

$$1 + 2\alpha\chi^2 + 2\alpha\xi = 4\alpha\chi + \xi^2.$$

It appears, therefore, to be impossible, or at any rate eminently unlikely, by means of any experiment, in which the decomposed or modified chlorine is passed into water or an aqueous solution, to pronounce an opinion as to the origin of the oxygen discovered by Meyer, or even, strictly speaking, to assert with certainty that the chlorine has been decomposed at all into heterogeneous substances.

The experiment, however, in which the residual chlorine was absorbed by metallic mercury, and which V. Meyer has several times repeated, is not open to these objections.

This critical experiment is as yet the sole, but yet may be sufficient, evidence of the decomposition of chlorine, and the formation of oxygen in that decomposition. As no gas but oxygen is formed, the other constituent of the chlorine must have combined with the mercury, and will there, we may hope, be discovered.

The proportion of oxygen collected in V. Meyer's experiments is, as before said, very small, not amounting to more than from $\frac{1}{2}$ to 1 per cent. of the chlorine decomposed, and when the chlorine was heated during its passage through a horizontal instead of, as usual, a vertical tube, no oxygen at all was found. If all the oxygen theoretically indicated could be collected, it would amount to 50 per cent. of that chlorine. This diminution may be explained by the recombination of the constituents of the chlorine when the temperature falls. This recombination would, we may assume, proceed very rapidly at first, and with much less rapidity when a large amount of chlorine had been reproduced, and the constituents of the chlorine thus protected from recombination by dilution with a gas by which they were not affected. The case is similar, as was pointed out to me by my friend Professsor G. G. Stokes, to the survival of a small amount of detonating gas in an atmosphere of water-vapour, in the well known lecture experiment in which steam is passed through a porcelain tube at an elevated temperature, or in the original experiment of Sir W. R. Grove, in which the vapour of water is passed through an incandescent tube of platinum, when a current of oxyhydrogen gas is obtained.* Again, when carbonic acid gas is decomposed by the passage of an electric spark through the gas in an ordinary eudiometer, the gas is decomposed into carbonic oxide and oxygen, but this decomposition only proceeds to a certain point, at which the proportion of carbonic acid having been greatly diminished, the gases suddenly recombine and the experiment recommences.†

* *Ann. Chem.* [3], **19**, 253.

† *Ann. Chem.*, **113**, 140.

Another reason which may be given for the small amount of oxygen collected is that it is possible that no greater amount of oxygen was ever formed. We might have two simultaneous decompositions of the chlorine occurring in very different proportions according to the equations already given—

$$1 + 2\alpha\chi'^2\xi^2 = 2\alpha\chi'^2\xi + \xi^2$$
$$1 + 2\alpha\chi'^2\xi^2 = 2\alpha\chi'^2\xi + (\chi'\xi)^2.$$

In the former decomposition oxygen would be formed, in the latter not, but the change in the volume of the chlorine would be the same in either case. Recombination, however, might occur in the latter case far more rapidly than in the former, so that the only products of the decomposition which would escape would be those produced in the former reaction.

Reverting to the case of the binoxide and tetroxide of nitrogen, if it be admitted that the change in the density of chlorine observed by V. Meyer be evidence of the decomposition of chlorine, it is impossible to resist the conviction that the change in the densities of those gases is also due to their decomposition. It is to be hoped that in the light of these new facts, these gases may at length be submitted to a thorough and critical examination.

LXVIII.—*Note on Safranine.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

This beautiful colouring matter was discovered by W. H. Perkin, F.R.S., who found that it is a bye-product of the manufacture of mauve, and formed by the oxidation of mauveine (*Proc. Roy. Inst.*, 5, 572). Some time afterwards we commenced an investigation on this subject, and prepared a quantity of safranine, by adding gradually manganese dioxide to a boiling solution of mauveine in dilute sulphuric acid, as long as any effervescence took place: we boiled then for some time until the solution had assumed a clear red colour, neutralised with sodium carbonate, and filtered. On the addition of common salt to the filtrate, impure safranine was precipitated.

The residue on the filter contained a purple colouring matter which we first supposed to be undecomposed mauve; but this is not the case, inasmuch as it does not yield safranine, but colourless oxidation-products.

The impure safranine to which this purple colour obstinately ad-

heres was purified by treating its concentrated solution with soda, filtering, throwing out with salt, and repeating these operations until the admixture was removed. The product thus obtained was, after recrystallisation from hot water, found to be neither a base nor a sulphate, but a chloride, which was further purified by recrystallisation from hot dilute hydrochloric acid. It forms beetle-green crystals, resembling strongly those of magenta.

While this investigation was going on, Hofmann and Geyger published a paper on commercial safranine, which, however, is not obtained from mauveine, but from orthotoluidine (*Deut. Chem. Ges. Ber.*, 5, 526). Now as mauveine is undoubtedly derived from pure aniline, it appeared very probable that the two safranines were not identical (Schorlemmer, "Carbon Compounds," 408). On the other hand, our product showed all the characteristic reactions of that examined by Hofmann and Geyger. The only difference that we could find was, that the chloride of commercial safranine forms, according to Hofman and Geyger, thin reddish crystals; and further that the analysis of our compound gave less carbon and hydrogen than required by the formula $C_{21}H_{21}N_4Cl$.

We did not then continue this research, but since E. and O. Fischer have found that homologous rosanilines exist, it appeared to us not improbable that this might also be the case with safranine, our body being the lower homologue of the compound obtained from orthotoluidine, and therefore having the formula $C_{20}H_{19}N_4Cl$. In fact our analytical numbers agree with this supposition:—

	Calculated.	Found.					
Carbon	68·47	67·92	67·86	—	—	—	—
Hydrogen ..	5·42	5·51	5·47	—	—	—	—
Nitrogen ..	15·98	—	—	15·38	—	—	—
Chlorine ..	10·13	—	—	—	10·34	9·90	9·82
	100·00						

The numbers obtained for carbon and hydrogen appear to be the most decisive, differing considerably from those of Hofmann and Geyger, who obtained the following results:—

	Calculated.	Mean found.
Carbon	69·14	68·52
Hydrogen	5·76	6·15
Nitrogen.....	15·36	15·17
Chlorine.....	9·74	9·98
	100·00	99·82

We are continuing this research in order to establish the true formula of safranine from mauveine, and also, if possible, to ascertain the constitution of these compounds.

LXIX.—*Suberic and Azelaïc Acids.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

A few years ago we published a note on suberone and α-pimelic acid, which is obtained by its oxidation (this Journal, 1874, 935). Since this time we have studied the action of phosphorus pentoxide, pentasulphide, and other agents on suberone, without, however, obtaining decisive results. Want of material obliged us to interrupt this research, which we are able to start again now, as we have got a good supply of suberic acid obtained from castor-oil by Arppe's method.

In each operation about 6 litres of nitric acid of sp. gr. 1·25 were placed in a bolt-head, which was connected, by means of a doubly-perforated cork, on one side with a long inverted Liebig's condenser, and on the other with the vessel containing the oil, and was provided at the bottom with a tubulus, by means of which the oil passed through an india-rubber tube and a long glass tube into the acid, the whole arrangement forming a syphon, which, by immersing the glass tube more or less deeply into the large flask, allowed the flow of the oil to be regulated. As soon as the acid began to boil, the castor-oil was slowly run in, when soon a violent reaction ensued, and so much liquid condensed in the cooled tube that the pressure temporarily prevented the oil running in. After some time the reaction moderated, and a further supply of oil produced again the same phenomena. Thus the reaction went on so regularly that it was hardly necessary to watch it. After about 24 hours the formation of red fumes ceased, and the operation was stopped. Of course the cork was also readily attacked, but one cork generally lasted for one operation.

In order to remove the oenanthylic acid which is formed at the same time, the product was distilled, with repeated addition of water, and the hot residual liquid poured off from a heavy nitrogenous oil. On cooling, a mixture of suberic and azelaïc acids separated out, which was recrystallised from boiling water. On dissolving it in ammonia and precipitating fractionally with calcium chloride, pure azelaïc acid may be easily obtained; but in order to get pure suberic acid, the extraction with ether is the only method yielding satisfactory results. Thus all the azelaïc acid, as well as the remainder of the nitrogenous oil

which obstinately adheres to it are easily removed, the residue consisting of suberic acid, crystallising from water in long needles or large plates.

The ethereal extracts left on evaporation impure azelaïc acid, which was purified by dissolving in boiling water and adding common salt as long as an oily liquid separated. On cooling the clear solution, azelaïc acid crystallised out, which was further purified by repeating the above treatment. The oil which is precipitated by salt carries down a considerable quantity of azelaïc acid, which is separated from it by repeating the process described. Thus pure azelaïc acid, crystallising in large needles or plates and melting at 106·5°, is obtained without much difficulty.

The oxidation of castor-oil is not a pleasant operation, and we therefore tried to obtain suberic acid also by oxidising a large quantity of cork-cuttings. At the same time we were anxious to examine the bye-products, which have hitherto never been carefully studied.

The cork was heated with about four times its weight of nitric acid of sp. gr. 1·3 until the organic tissue was almost completely destroyed, which required about 36 hours. The hot solution was then separated from a brown wax-like matter and the remaining cellular substance by filtering through a cloth. The filtrate contained, besides suberic acid, also *a large quantity of azelaïc acid*, as well as oxalic acid and different other compounds, which have not yet been examined.

The oxidation of castor-oil and cork has been carried out quite independently by Mr. Spiegal, to whom our best thanks are due for the great zeal and ability with which he has done this work.

The preparation of pure suberone offers no difficulties. It does not appear necessary to prepare first calcium suberate, as a mixture of suberic acid with excess of slaked lime gives the same yield of the crude product, containing always a little normal hexane, and a not inconsiderable quantity of a liquid boiling at a very high temperature, and leaving fatty matters on distillation. The chief products, however, consist of pure suberone, which is obtained by a few fractional distillations as a colourless liquid, boiling at 179—181°, and smelling like peppermint.

Its analysis and determination of the vapour-density gave the following results:—

Substance.	CO_2.	H_2O.
0·341	0·943	0·345

	Calculated.		Found.
C_7	84	75·00	77·4
H_{12}	12	10·71	11·2
O	16	14·29	—
	112	100·00	

Weight of suberone	0·0685
Temperature of air	16·5°
Temperature of vapour	185°
Volume of vapour	115 c.c.
Atmospheric pressure	758 mm.
Height of mercury in the tube	606·5 mm.

Vapour-density calculated.	Found.
3·87	3·73

On heating suberone with common nitric acid, a violent reaction sets in, and an oil, having a pungent smell, is first formed. This is probably an aldehyde of α-pimelic acid, which is produced by further oxidation. It crystallises from hot water in large, rectangular, rhombic plates (this Journal, 1874, 937), and melts, if perfectly pure, at 100°, as A. Baeyer found, who obtained the same acid from furfurol and acetic anhydride (*Deut. Chem. Ges. Ber.*, **10**, 1358). Its analysis gave the following results:—

Substance.	CO_2.	H_2O.
0·1525	0·2927	0·1032
0·2920	0·5590	0·2020

	Calculated.		Found.	
C_7	84	52·5	52·34	52·20
H_{12}	12	7·5	7·51	7·68
O_4	64	40·0	—	—
	160	100·0		

Silver pimelate, $C_7H_{10}Ag_2O_4$, is a heavy white precipitate, which is sparingly soluble in boiling water, and not affected by light.

0·3090 left on ignition 0·1790 Ag.

Calculated.	Found.
57·75	57·83

Calcium pimelate, $C_7H_{10}CaO_4$, dissolves much more freely in cold than in hot water, and therefore separates on boiling its cold saturated solution, as a granular, flocculent powder, which, if the solution has not become too concentrated, re-dissolves gradually on cooling. By spontaneous evaporation it is obtained as a white, light, crystalline

mass, which apparently is not wetted by water, but when left in contact with it dissolves completely after some time.

0·082 left on ignition 0·323 CaO.

	Calculated.	Found.
Ca	20·2	20·0

Barium pimelate, $C_7H_{10}BaO_4 + H_2O$, is freely soluble in water, and crystallises in transparent plates, which seem to belong to the rhombic system.

0·1925 lost on heating 0·0130 H_2O, and the residue left on ignition 0·1200 $BaCO_3$.

	Calculated.	Found.
H_2O.....	5·75	6·75
Ba	46·44	46·48

As suberone is so easily obtained, we intended to prepare also its next homologue from azelaïc acid, and therefore subjected a mixture of it with slaked lime, as well as pure calcium azelate, to dry distillation. In both cases a good yield of a liquid was obtained, which melted like crude suberone, but was found to be a most complicated mixture from which no definite compound could be isolated. It began to boil at about 100°, the boiling point of normal heptane; the temperature then rose gradually above 360°, and a considerable quantity of a tarry matter was left behind. After a continued fractional distillation, a comparatively large portion distilled between 180—220°; it melted like suberone, but it was impossible to isolate either this compound or any other having a constant boiling point. On heating it with nitric acid we obtained nitro-compounds and a crystalline acid, which we examined as far as the small quantity which was produced allowed us to do. We found that it was neither oxalic nor succinic acid, but probably a mixture of higher homologues of this series.

We also distilled suberic acid with lime; the results were almost the same as in the case of azelaïc acid, the only difference being that the distillate began to boil at 124°, or the boiling point of normal octane.

From this we must conclude that suberic acid is not analogous in constitution to its two higher homologues. We have already pointed out that the former appears to be a normal compound. This view finds support in Baeyer's synthesis of α-pimelic acid, and in the fact that by the action of silver-dust on bromobutyric and on bromoisobutyric acids, isomerides of common suberic acid are formed (Hell, (*Deut. Chem. Ges. Ber.*, **6**, 28; Hell and Wittekind, *ibid.*, **7**, 319). Moreover, Toennies (*ibid.*, **12**, 1200) has shown that from furfurol and normal butyric anhydride an azelaïc acid can be obtained, which is undoubtedly the true homologue of α-pimelic acid, but quite different

from the hitherto known azelaïc acid. We shall endeavour to ascertain the constitution of the latter, although this subject probably offers great difficulties, inasmuch as theory predicts the existence of 12 isomerides, of which each ought to yield heptane when distilled with baryta. In the case of sebacic acid the number of isomerides, which by the removal of carbon dioxide would be converted into normal octane, is of course still larger.

LXX.—*On Gardenin.*

By J. Stenhouse, F.R.S., and Charles E. Groves.

A short note on this substance was published in the Society's Journal some time ago (1877, i, 551), in which we described a method of extracting it from the so-called "Dekamali gum," the resinous exudation from the *Gardenia lucida*. We also stated that a compound of a red colour might be obtained from gardenin by the action of nitric acid, but that the amount of material at our disposal was too small to permit of a thorough examination. Since then we have succeeded in obtaining a considerable quantity of the resin from India, which has enabled us to continue our investigations.*

Extraction of the Gardenin.

The resin of the *Gardenia lucida* has a peculiar and unpleasant alliaceous odour, which is undoubtedly due to some volatile compound. The possession of a comparatively large quantity of freshly collected resin (1 cwt.) afforded a favourable opportunity for ascertaining the nature of this substance. The resin was accordingly broken up into small pieces, introduced into a copper vessel, and the volatile oil distilled off in a current of steam. The quantity was very small, however, only about 100 c.c. of the oil being obtained from the cwt. of resin. Curiously enough, neither the volatile oil which distilled over along with the water, nor the resinous residue in the copper still, had any marked alliaceous odour. When oil ceased to come over with the

* The resin may be easily procured in Bombay, the cost there being about four pence per lb.: the resin differs considerably in quality, however, some specimens containing much more earthy and woody matter than others; but in all cases the amount of gardenin present is but small, being only about 1 to 1·4 per cent. As might be supposed, the resin if old yields only a very small quantity of volatile oil on distillation with water.

water, the distillation was stopped, the still opened, and the residue removed while still hot. It was then allowed to stand for 12—24 hours to harden, and the water present was removed as far as possible by means of a centrifugal machine. Eight parts of the resin, which may have been distilled with water or not, are boiled with 15 parts of spirit for 3—4 hours, and then filtered while hot through a bag-filter to retain the woody and sandy matter. The residue is then treated a second, third, and fourth time with 10 parts of spirit in a precisely similar manner, the insoluble woody residue being finally dried in a centrifugal machine, in order to recover as much of the spirit as possible. The third and fourth extracts, after being filtered from the gardenin which has crystallised out, are used instead of pure spirit for treating a fresh quantity of the resin, whilst the first and second extracts are placed in a bottle and left for 14—20 days, at the end of which time the crystallisation of the gardenin is completed. As the alcoholic solution is somewhat viscous from the large quantity of resin dissolved in it, and the gardenin crystals are accompanied by a considerable amount of a fatty or waxy matter which quickly stops up the filters, there is some difficulty in collecting it: the best method is to employ a Taylor's filter of close twilled cotton, using a pressure tube 10—12 feet long. On concentrating the alcoholic mother-liquors, and allowing them to stand some months, no further quantity of gardenin is deposited, the traces which are present being in all probability prevented from crystallising by the resin which is in solution. In order to remove the alcoholic resinous solution adhering to the pasty mass of fat and gardenin which remains in the bag-filter, and which would greatly interfere with the subsequent purification of the product, it is stirred up with 5 parts of spirit for each 8 parts of resin originally taken, collected again in the bag-filter, and washed a second time in a similar manner with spirit. The product is finally pressed strongly to remove as much of the alcohol as possible. These alcoholic washings can be used instead of clean spirit in the extraction of fresh quantities of resin. The greenish-yellow cake of gardenin and fat obtained in this way is broken up, and after being dried at the ordinary temperature or at a very gentle heat, is dissolved in six times its weight of boiling benzene, and filtered hot. In this way a solution is obtained containing gardenin mixed with waxy or fatty matter, and on cooling the two crystallise out together. In order to separate them, the benzene is completely removed by distillation in a current of steam, and the residue, after being dried, is treated several times successively with boiling light petroleum until the fat is removed. The nearly pure gardenin, after the petroleum adhering to it has evaporated, is recrystallised once or twice from benzene (12 parts) and from spirit (60 parts).

When large quantities of substance have to be operated on, the use of petroleum to remove the whole of the fat is inconvenient, and attended with some risk. This may be to a great extent avoided by treating the pressed cake of mixed gardenin and fat with hot dilute ammonia. For this purpose the cake from 8 parts of resin is broken into small pieces and boiled with 8 parts of dilute ammonia (containing 2 per cent. of ammonia solution, sp. gr. 880) until it is thoroughly disintegrated, which usually takes about ten minutes. It is then left for about 30 minutes for the bulk of the gardenin to settle, and the supernatant liquid decanted while still hot. The gardenin which is almost free from fat is then washed by decantation with a little hot water, collected, dried, and at once purified by crystallisation from benzene (12 parts) and spirit. The liquid decanted from the gardenin, when left at rest for 24 hours, deposits a further quantity of gardenin with some waxy and fatty matter, which cannot be separated by treatment with ammonia, and after being washed, collected, and dried, must be exhausted with petroleum before being crystallised from benzene. The turbid yellowish ammoniacal mother-liquors, on being neutralised with an acid, yield a curdy precipitate of fat containing traces of gardenin. By adopting this process, three-fourths of the total quantity of gardenin is obtained at once in a nearly pure state; and although it is necessary to treat the remainder with petroleum, &c., to remove the fat, a great saving of time and labour is effected, and the risk considerably diminished.

Before being analysed, the gardenin was crystallised from boiling chloroform (4 parts), and subsequently from boiling spirit (60 parts). Purified in this manner, the gardenin had the same melting point, 163—164°, as that previously found by us, and when burnt in a current of oxygen, gave the following numbers:—

I. 0·169 gram substance gave 0·377 gram carbonic anhydride and 0·072 gram water.

II. 0·218 gram substance gave 0·485 gram carbonic anhydride and 0·093 gram water.

III. 0·207 gram substance gave 0·435 gram carbonic anhydride and 0·089 gram water.

				I.	II.	III.	Mean.
C_{14}	=	168	60·87	60·84	60·68	61·00	60·85
H_{12}	=	12	4·35	4·74	4·74.	4·78	4·75
O_6	=	96	34·78	—	—	—	34·40
		276	100·00				

These numbers agree fairly well with the formula $C_{14}H_{12}O_6$, but this point cannot be considered as definitely settled until its derivatives have been more carefully investigated.

Terpene from Gardenia lucida.

The volatile oil extracted from the Dekamali gum by distilling it in a current of steam, when submitted to fractional distillation, begins to boil at 140°, but the temperature rapidly rises to 160°. Between 160° and 170° more than half the oil comes over; the temperature then rises very quickly to 255°, where it remains almost stationary until nearly the whole has come over. A small quantity of a dark olive-brown liquid is left in the retort, having an aromatic but slightly alliaceous odour. On examination, it is found to contain a trace of sulphur. By successive fractionations, the last of which must be made over metallic sodium, more than half the total quantity of oil may be obtained in a nearly pure state, boiling between 157° and 160°. Of this a large proportion boils constantly at 158°, and was submitted to analysis. It gave the following results :—

I. 0·255 gram substance gave 0·824 gram carbonic anhydride and 0·277 gram water.

II. 0·166 gram substance gave 0·537 gram carbonic anhydride and 0·179 gram water.

			I.	II.	Mean.
C_{10}	120	88·24	88·13	88·23	88·18
H_{16}	16	11·76	12·07	11·98	12·02
	136	100·00			

The larger portion of the oil, therefore, is of the nature of a terpene. During the rectification, a portion of oil was separated boiling at about 250°, but the quantity was too small to enable us to purify it sufficiently for analysis.

Gardenic Acid.

As already mentioned, one of the products of the action of nitric acid on gardenin is a red crystalline substance, insoluble in water and in dilute acids, but readily soluble in alkaline solutions, and provisionally named *gardenic acid*. This compound may be obtained in various ways, as by the addition of nitric acid to a hot concentrated alcoholic or glacial acetic acid solution of gardenin, or by the action of dilute nitric acid on gardenin in the cold. When a small quantity of nitric acid is added to a boiling concentrated solution of gardenin in spirit, the solution becomes red, and in the course of a minute or two solidifies to a pulp of minute orange-red needles, consisting of gardenic acid, mixed, however, with more or less of an amorphous brown-red substance. A much purer product is obtained on substituting glacial acetic acid for alcohol; 1 part of pure gardenin is dissolved in 20 of

boiling glacial acetic acid, and the solution is rapidly cooled, taking care, however, that the gardenin does not crystallise out, but remains dissolved as a supersaturated solution. 1 part by weight of nitric acid, sp. gr. 1·45, diluted with its own bulk of acetic acid, is then poured into the gardenin solution, and the liquid, which becomes of a deep-red colour, is agitated strongly while kept cool: in a very short time crystals begin to make their appearance, and the whole becomes a pasty mass of red needles. In 5—8 minutes, after the nitric acid has been added, the reaction is complete; 100 parts of water are then added, and the product is at once collected on a vacuum filter. As soon as all the liquid has passed through, the filter should be removed from the platinum cone, and the product washed out and stirred up thoroughly with 50 parts of water; then left for 10 minutes and collected. It is then again washed with 50 parts of water in a precisely similar manner, except that it is left at rest for 20—30 minutes before collecting. The product should be removed from the filter by gently pressing it together, and the crystalline cake dried at a gentle heat. The crude substance amounts to 80—85 per cent. of the weight of the gardenin operated on. As gardenic acid readily decomposes when left in contact with nitric acid, it is necessary that it should be separated from the mother-liquor as quickly as possible. On this account it is not advisable to operate on more than 2 grams of gardenin at a time; otherwise the time occupied in collecting the product on an ordinary vacuum-filter would be long enough for partial decomposition to take place.

Gardenic acid may also be conveniently prepared from gardenin by the action of dilute nitric acid alone, without the use of glacial acetic acid. 1 part of gardenin in a fine state of division is placed in a beaker immersed in cold water, and 10 measures of nitric acid, sp. gr. 1·25, are poured on it, the mixture being well stirred. The gardenin almost immediately acquires a deep orange tint, and in the course of three or four minutes solidifies to a paste of bright red needles of gardenic acid. The reaction is complete in ten minutes, and the pasty product should then be at once collected on a vacuum-filter, and washed, first with a little of the diluted nitric acid, sp. gr. 1·25, and subsequently with water. The last traces of nitric acid are removed by washing twice with water in a manner precisely similar to that previously described for the glacial acetic acid method, the yield obtained being about the same.

The crude gardenic acid prepared by either of the above mentioned processes contains a small quantity of a brown amorphous substance, and must be purified by crystallisation from boiling chloroform, in which, however, it is only very sparingly soluble. It forms beautiful deep crimson needles, which begin to decompose, and melt at about

223°, but the fusion point is not sharply defined. It is insoluble in water, light petroleum, and carbon bisulphide, and almost insoluble in ether or benzene. It dissolves readily in cold dilute alkaline solutions with a deep yellow colour, and is reprecipitated on addition of an acid. Dried at 100° and burnt in a current of oxygen, it gave the following results :—

I. 0·209 gram substance gave 0·463 gram carbonic anhydride, and 0·081 gram water.

II. 0·2235 gram substance gave 0·4935 gram carbonic anhydride, and 0·086 gram water.

			I.	II.	Mean.
C_{14}	168	61·31	60·42	60·22	60·32
H_{10}	10	3·65	4·31	4·27	4·29
O_6	96	35·04	—	—	—
	274	100·00			

The formula of this substance cannot be regarded as settled, and although we have retained the name "gardenic acid," which was provisionally assigned to the product of the action of nitric acid on gardenin, we consider it to be very improbable that it actually has the constitution of an organic acid, that is to say that it contains the group COOH, its behaviour with reducing agents and with alkaline solutions pointing rather to a quinone grouping.

Gardenic acid dissolves in cold nitric acid, sp. gr. 1·45, giving a dark brown solution, which does not yield any precipitate on addition of water, and when heated becomes of a pale yellow colour. When gardenic acid is left in contact with dilute nitric acid for a considerable length of time, gas is evolved, and it is converted into a substance of a bright orange colour, which under the microscope is seen to consist of colourless crystals, mixed with an orange-coloured, amorphous substance; on boiling the mixture with water, the colourless crystals dissolve, leaving the orange amorphous substance. If the mixture of gardenic acid with dilute nitric acid is heated instead of being left in the cold, it effervesces strongly, and, on cooling, the solution deposits long colourless needles. This substance is very soluble in alcohol, but only sparingly soluble in cold water, or in dilute alkaline solutions; it appears to be identical with the colourless crystals mentioned above.

Acetylgardenic Acid.

When crude gardenic acid is boiled for some time with glacial acetic acid, in which it is easily soluble, and crystallised once or twice from that solvent, it becomes more orange-coloured, and the melting point is considerably raised. The new acetyl-derivative may be conveniently

prepared by boiling dry crude gardenic acid with 20 parts of glacial acetic acid for two hours, and allowing it to crystallise without previous filtration; the crystals are collected, washed with a little acetic acid, dissolved in 32 parts of the acid, and filtered. The acetylgardenic acid deposited from this solution on cooling is pure. It gave the following results on analysis:—

I. 0·194 gram substance gave 0·428 gram carbonic anhydride and 0·077 gram water.

II. 0·186 gram substance gave 0·413 gram carbonic anhydride and 0·073 gram water.

III. 0·207 gram substance gave 0·458 gram carbonic anhydride and 0·076 gram water.

				I.	II.	III.	Mean.
C_{18}	=	216	60·34	60·17	60·56	60·34	60·36
H_{14}	=	14	3·91	4·41	4·36	4·08	4·28
O_8	=	128	35·75	—	—	—	—
		358	100·00				

These numbers correspond with the formula $C_{18}H_{14}O_8$ or $C_{14}H_8(C_2H_3O_2)O_6$, that of *diacetylgardenic acid.*

Pure acetylgardenic acid crystallises from glacial acetic acid in long, slender, lustrous needles of a bright orange-red colour, which begin to darken at 230° and are completely melted at about 244°. The melting point is not sharply defined, as the substance evidently begins to decompose before it fuses. It is insoluble in water, light petroleum, and carbon bisulphide; almost insoluble in ether and benzene. It is only very slightly soluble in boiling alcohol, but dissolves in boiling chloroform and glacial acetic acid, and crystallises out again on cooling.

Acetylgardenic acid dissolves in dilute soda-solution with a purplish-red colour, which changes to orange-red on boiling: the addition of an acid to this solution throws down a flocculent precipitate of a deep orange colour, which may be obtained in the crystalline state from glacial acetic acid. It has not as yet been further examined. Acetylgardenic acid dissolves in cold concentrated sulphuric acid, yielding a dark-brown solution in which water produces a red amorphous precipitate. If the quantity of water added is not greater than the bulk of the sulphuric acid, this amorphous precipitate redissolves on heating the mixture, and the deep-red solution deposits red crystals on cooling.

Hydrogardenic Acid.

When gardenic acid is left in contact with an aqueous solution of sulphurous acid, it becomes of a brilliant yellow colour, and is con-

verted into a new compound containing more hydrogen than gardenic acid. The gardenic acid obtained by one of the methods already described, is introduced into a flask whilst still moist, together with a concentrated solution of sulphurous acid, and the two are thoroughly mixed by repeated agitation. After standing for 24 hours, the gardenic acid will be found to be completely converted into a somewhat gelatinous paste of a bright yellow colour. This is collected, washed with water, pressed to remove as much of the water as possible, and dissolved in the smallest possible quantity of boiling spirit. On cooling, the hydrogardenic acid crystallises out, and may be rendered quite pure by recrystallisation from spirit. Pure hydrogardenic acid crystallises in flat, lustrous needles, which, when dry, closely resemble lead iodide in colour and appearance. It melts at 190°, and is insoluble in water, light petroleum, and carbon bisulphide, sparingly soluble in ether, but readily in hot benzene, spirit, or glacial acetic acid. When cautiously treated with oxidising agents, it is reconverted into gardenic acid. Hydrogardenic acid dissolves readily in dilute soda-solution with a pale orange-red colour, and on addition of an acid a yellow flocculent precipitate is produced consisting apparently of unaltered hydrogardenic acid. If, however, the alkaline solution is boiled, it rapidly acquires a purple colour, and on adding an acid, now yields a yellow precipitate differing in appearance and properties, both from the original substance, and also from that obtained in alkaline solutions of gardenic acid. The analyses of hydrogardenic acid dried at 100° gave the following results:—

I. 0·185 gram substance gave 0·410 gram carbonic anhydride and 0·091 gram water.

II. 0·185 gram substance gave 0·412 gram carbonic anhydride and 0·088 gram water.

III. 0·203 gram substance gave 0·450 gram carbonic anhydride and 0·092 gram water.

				I.	II.	III.	Mean.
C_{14}	=	168	60·43	60·44	60·74	60·46	60·55
H_{14}	=	14	5·04	5·46	5·29	5·04	5·26
O_6	=	96	34·53	—	—	—	—
		278	100·00				

When gardenin is boiled for some time with stannous chloride, it is converted into a substance closely resembling the original gardenin in crystalline form and physical character, but differing greatly from it in its solubility. We have succeeded in preparing acetyl and benzoyl-derivatives of gardenin, but attempts to prepare halogen-derivatives of gardenin resulted in the formation of resinous bodies which resisted all efforts to obtain them in a crystalline state. As the yellow gar-

denin contains the hydroxyl group, it was thought possible that it might resemble the coloured substances obtained from the plants allied to madder: on heating it with zinc-dust, however, unsatisfactory results were obtained, only a very small quantity of an oily hydrocarbon being produced.

We intend to continue our study of gardenin and its derivatives, and hope before long to be able to lay before the Society another communication on the subject.

LXXI.—*On the Heat of Formation of Aniline, Picoline, Toluidine, Lutidine, Pyridine, Dipicoline, Pyrrol, Glycerin, and Furfurol.*

By William Ramsay, Ph.D., Tutorial Assistant of Chemistry in the University of Glasgow.

In a recent paper on the "Volumes of Liquids at their Boiling Points, obtainable from Unit-volumes of their Gases" (p. 463 of this volume), I remarked that some connection might exist between the "ebullition-volume" of a liquid and the amount of heat evolved during its formation. The experiments to be described were undertaken to ascertain whether any relation could be discovered.

It is evidently impossible to determine directly the heat of formation of substances such as those mentioned in the title of this paper. The reactions which give rise to them are by no means neat, for numerous by-products are formed, and the yield is far from what theoretical considerations would lead us to infer. The indirect method has, therefore, to be used, the principle of which is as follows:—

The heat of combustion of compounds of carbon is an ascertainable quantity. It is also known what amount of heat would be evolved by the elements of which the substance is composed (carbon and hydrogen) were they to oxidise in the free state. But the heat evolved by the oxidation of the compound is not the same as that evolved by the oxidation of the elements of which the compound is composed, taken in the same proportion; it is considerably less. The difference between the two amounts of heat evidently represents the heat absorbed in decomposing the compound before its constituent elements are capable of being oxidised. In other words, the compound does not burn as a compound, but splits up into its elements, which then burn as elements; it absorbs heat, therefore, in decomposing. Now it is assumed that the heat required to decompose a compound is equal

to that heat evolved by it during its formation: therefore, by determining the heat of combustion of a substance containing carbon, its heat of formation may be indirectly inferred.

The apparatus used was that devised by Mr. Lewis Thomson for determining the heating power of fuel. It consists of a copper bell-jar, the upper end of which terminates in a copper tube provided with a stop-cock. A copper receiver, about 4 inches long and half an inch in diameter, contains the substance to be oxidised, mixed with about twelve times its weight of a mixture of 1 part of potassium nitrate and 3 parts of potassium chlorate. A cotton-fuse, prepared by soaking wick in a solution of lead nitrate, is inserted in the mixture and set on fire. The receiver is then placed in the bell-jar, and the whole is immersed in a known weight of water at a known temperature. Bubbles of gas are soon evolved, the substance is oxidised, and the rise of temperature of the water affords a datum from which the heat of combustion may be calculated. The thermometer used was read to $\frac{1}{100}$ of a degree.

In practice it was found that the oxidising mixture of 3 parts of potassium chlorate with 1 part of potassium nitrate, when mixed with organic liquids, could not be ignited. It was therefore necessary to add some substance to promote combustion, and the one which proved most convenient was sulphur. The amount of heat evolved by the combustion of a given weight of sulphur was consequently determined.

The ordinary mixture was mixed with $\frac{1}{16}$ of its weight of sulphur; this proportion proved sufficient to induce the combustion of the mixture in presence of an organic liquid. To ascertain the amount of heat evolved by the combustion of this sulphur, the following experiments were made:—

I. *Sulphur.*

A. Taken, 0·5 gram.
Mixture, containing $\frac{1}{16}$ of its weight of sulphur, 10 grams.
Rise of temperature of 1880 grams of water:—

Average of 6 experiments		1·64°
Probable error	„	± 0·029

B. Taken, 1 gram.
Mixture, 10 grams.
Rise of temperature:—

Average of 6 experiments		2·28°
Probable error	„	± 0·036

Rise of temperature with 1 gram of added S				2·28°
„	„	0·5	„	1·64
„	„	0·5	,	0·64

To calculate the heat evolved by combustion of the amount of sulphur originally present in the oxidising mixture (= 0·62 gram),

$$\frac{0{\cdot}64^\circ \times 0{\cdot}62 \text{ gram}}{0{\cdot}5 \text{ gram}} = 0{\cdot}79^\circ.$$

Subtracting that from the total amount of heat evolved by combustion of 1·62 gram of sulphur—

$$2{\cdot}28^\circ - 0{\cdot}79^\circ = 1{\cdot}49^\circ \text{ per gram of S; and}$$
$$1{\cdot}64 - 0{\cdot}79 = 0{\cdot}85 \text{ per half gram of S.}$$

But 1·49° is not equal to 0·85° × 2; the difference, however, lies within the limits of probable error: consequently a correction must be made, thus:—

		Heat evolved.	Probable error.	Sum.
0·62 gram S + 1 gram	= 1·62 gram	2·28°	+ 0·029	= 2·31°
0·62 „ + 0·5 „	= 1·12 „	1·64	− 0·029	= 1·61

0·5 gram sulphur therefore evolves 0·70

and the heat evolved by the combustion of the sulphur originally present in the mixture = 0·62 gram is

$$\frac{0{\cdot}62 \text{ gram} \times 0{\cdot}70^\circ}{0{\cdot}5 \text{ gram}} = 0{\cdot}87^\circ.$$

Now 2·31° − 0·87° = 1·44° per gram sulphur,
and 1·61 − 0·87 = 0·74 per half gram sulphur.

It was necessary to know accurately the amount of heat evolved by the original sulphur in the mixture: hence the care taken in determining it. Calculated to heat-units, these numbers give 2800 cal. as the amount of heat evolved by the combustion of 1 gram of sulphur.

From determinations by a different method—

1 gram SO_2	= 2220 cal.
1 gram $SO_2.O$	= 502 „
	2722

To that number must be added the heat evolved by the decomposition of potassium chlorate sufficient to oxidise the sulphur—

$$2722 + 240 = 2962 \text{ cal.}$$

This sulphuric anhydride, without doubt, reacts on the salts present (KNO_3, $KClO_3$, KCl), giving rise to other heat-phenomena, which it is impossible to follow out theoretically.

The numbers stand thus:—

Found for 1 gram S	2800 cal.
Calculated for S to SO_3	2962 „

II. *Aniline.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams water 2·57°
Probable error of 6 experiments ± 0·056
0·62 gram of sulphur present evolves 0·87.
2·57° − 0·87° = 1·70°, due to aniline alone.

This corresponds to evolution of 6390 cal.
1 gram aniline contains—

0·774 gram carbon, evolving	6037 cal.
0·075 „ hydrogen „	2564 „
Elements of aniline evolve	8601 „

The potassium chlorate required to oxidise the carbon and hydrogen of the aniline amounts to 6·787 grams, and absorbs 536 cal. in decomposing. 6390 cal. −536 cal. =5854 cal., evolved by combustion of aniline.

The C and H, however, should evolve	8601 cal.
The aniline evolved	5854 „
Heat absorbed in decomposing aniline	2747 „

This heat also represents the heat of formation of aniline.

III. *Picoline.*

Taken, 0·5 gram.
Mixture, 10 grams.
Average rise of temperature of 1880 grams of water 1·77°
Probable error of 6 experiments ± 0·030

1·77° − 87° (heat evolved by sulphur present) = 0·90°, due to picoline alone, corresponding to 3384 cal.

As aniline and picoline are isomerides, the numbers given in (II) are applicable.

3384 cal. − 536 cal. = 2848 cal. evolved by picoline.

The C and H should evolve	8601 cal.
The picoline evolves	2848 „
Heat absorbed in decomposing picoline	5753 „

Or, 5753 cal. are evolved during formation of picoline.

IV. *Toluidine.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams water = 3·07°
Probable error of 6 experiments = ± 0·022
3·07° − 0·87° (heat evolved by sulphur) = 2·20°.
Corresponding to 8272 cal. per gram of toluidine.

1 gram of toluidine contains—

0·785 gram carbon, evolving	6123	cal.
0·084 „ hydrogen „	2872	„
Elements of toluidine evolve	8995	„

Potassium chlorate required to oxidise 1 gram toluidine = 7·064 grams evolving 558 cal.

Heat evolved from toluidine + $KClO_3$,	8272	cal.
„ „ $KClO_3$	558	„
	7714	„

8995 cal. − 7714 cal. = 1281 cal. absorbed by decomposition, or evolved by formation of toluidine.

V. *Lutidine.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams water = 1·50°
Probable error of 6 experiments = ± 0·044
1·50° − 0·87° = 0·63°, corresponding to 2369 cal. per gram.

Heat evolved by constituent carbon and hydrogen 8995 cal.
2369 cal. (from lutidine) −558 cal. (from $KClO_3$) = 1811 „
Heat evolved by formation of lutidine = 7184 „

VI. *Pyridine.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams water = 1·26°
Probable error of 6 experiments = ± 0·051
1·26° − 0·87° = 0·39°, corresponding to 1466 cal. per gram.
1 gram of pyridine contains—

0·759 gram carbon, evolving	5920	cal.
0·063 „ hydrogen „	2153	„
Elements of pyridine evolve	8073	„

Potassium chlorate required to oxidise 1 gram pyridine = 6·456 grams, evolving 510 cal.

Heat evolved from pyridine	+	$KClO_3$ =	1466 cal.
,, ,,		$KClO_3$ =	510 ,,
			956 ,,

8073 cal. − 956 cal. = 7117 cal. evolved by formation of pyridine.

VII. *Dipicoline.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Rise of temperature of 1880 grams water (1 expt.) = 1·15°
1·15° − 0·87° = 0·28°, corresponding to 1053 cal. per gram.

Elements of dipicoline (same as picoline) evolve 8601 cal.
Potassium chlorate required to oxidise 1 gram dipicoline = 6·787 grams, evolving 536 cal.

Heat evolved from dipicoline	+	$KClO_3$ =	1053 cal.
,, ,,		$KClO_3$ =	536 ,,
			517 ,,

8601 cal. − 517 cal. = 8084 cal., evolved by formation of dipicoline.

VIII. *Pyrrol.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams of water 2·16°
Probable error of 6 experiments 0·043

2·16° − 0·87° = 1·29°, corresponding to 4850 cal. per gram.
1 gram of pyrrol contains—

0·7164 gram carbon evolving		5851 cal.
0·0746 ,, hydrogen ,,		2550 ,,
		8401 ,,

Potassium chlorate required to oxidise 1 gram pyrrol = 6·403 grams, evolving 505 cal.

Heat evolved from pyrrol	+	$KClO_3$ =	4850 cal.
,, ,,		$KClO_3$ =	505 ,,
			4345 ,,

8401 − 4345 = 4056 cal. evolved by formation of pyrrol.

IX. *Glycerin.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams water = 2·30°
Probable error of 6 experiments = 0·031

2·30° − 087° = 1·43°, corresponding to 5376 cal. per gram.
1 gram of glycerin contains—

0·391 gram carbon evolving	3050 cal.
0·087 „ hydrogen, of which $\frac{3}{4}$ is burned by oxygen contained in glycerin, 0·021 remains	718 „
	3768 „

Potassium chlorate required to oxidise 1 gram of glycerin = 3·093 gram, evolving 244 cal.

Heat evolved from glycerin + $KClO_3$ =	5376 cal.
„ „ $KClO_3$ =	244 „
	5132 „

3718 cal. − 5133 cal. = −1364 evolved by formation of glycerin, or 1364 cal. absorbed.

X. *Furfurol.*

Taken, 0·5 gram.
Mixture, 10·0 grams.
Average rise of temperature of 1880 grams of water 0·93°
Probable error of 6 experiments 0·019

3·93° − 0·87° = 0·06°, corresponding to 225 cal. per gram.
1 gram of furfurol contains—

0·6250 gram carbon evolving 4875 cal.
0·0416 „ hydrogen already oxidised.

Potassium chlorate required to oxidise 1 gram of furfurol = 4·257 gram, evolving 336 cal.

Heat evolved from furfurol + $KClO_3$ =	225 cal.
„ „ $KClO_3$ =	336 „
	111 „

4875 cal. + 111 cal. = 5985 cal. evolved by formation of furfurol.

Such are the results obtained by experiment; it now remains to tabulate them:—

	Cal. evolved.		Cal. evolved.
Aniline	2747	Toluidine	1281
Picoline.....	5753	Lutidine.....	7184
Dipicoline.....	8084	Pyridine.....	7117
Glycerin	−1364	Pyrrol	4056
Furfurol	5985		

The probable divergence from these numbers is very small, but is calculable from the probable error.

In comparing aniline with picoline, it is to be remarked that picoline evolves more than twice as much heat during formation as aniline, and lutidine six times as much as toluidine.

In the aniline series addition of CH_3 appears to be accompanied by absorption of heat; on the other hand, lutidine may be a starting point for a new series, for a difference of CH_3 has a totally different effect.

Dipicoline, as might be expected, evolves heat during its formation from picoline; but it is remarkable to observe that pyridine and lutidine so nearly coincide.

Turning to the oxygenated compounds, it is seen that glycerin absorbs heat during formation, while furfurol evolves heat. Whether this is a constant property of alcoholic and aldehydic oxygen is a matter for further research. Berthelot has recently shown that cyanogen absorbs heat during formation; but many experiments are required before a connection between different members of a series can be established.

In conclusion, I would remark two sources of error, which may influence the above results, or indeed any results obtained by a similar method; they are unfortunately very difficult, if not impossible, to eliminate in the present state of our knowledge. In the first place, it is assumed that, in an act of chemical combination, all, or at least a constant proportion of the energy, is evolved or absorbed in the form of heat; and secondly, the heats of combination of carbon and hydrogen with oxygen are assumed to be the same when in the state of elements as when in the nascent state. This is a pure hypothesis, for it is by no means improbable that free carbon in burning absorbs a certain amount of heat in, so to speak, dissociating from itself, whereas when a compound is dissociated, absorbing heat during the process, no heat is lost in decomposing the carbon molecules, for the carbon is in the act of separating from hydrogen, or from other elements.

LXXII.—*On the Atomic Weight of Tellurium.*

By W. L. Wills, B.Sc., Student in the Owens College Chemical Laboratories.

The atomic weight of tellurium has been determined twice; in the first place by Berzelius, and secondly by von Hauer. The former (*Pogg. Ann.*, 1834, **32**, 16) oxidised a known weight of tellurium with dilute nitric acid, and weighed the dioxide formed, obtaining the numbers 128·13, 127·96, and 127·95 (O = 15·96). Berzelius calculated his number from the latter two experiments which give Te = 127·955. The method employed by him for purifying his tellurium was that of distilling in hydrogen the tellurium obtained from potassium telluride. Subsequently von Hauer (*J. pr. Chem.*, 1858, **72**, 98) determined the atomic weight of tellurium by the analysis of a double bromide of tellurium and potassium, the amount of bromine in the salt being ascertained by precipitation with silver nitrate. As a mean of five experiments varying between Te = 126·86, and = 128·49, von Hauer obtained the number 127·74 as the atomic weight of tellurium (Br = 79·75, K = 39·04).

Dumas (*Ann. Chem. Pharm.*, 1860, **113**, 30) from experiments not published in detail, concludes that Te = 129.

Deville and Troost (*Compt. rend.*, **56**, 871) determined the density of tellurium vapour as 9·00 at 1390°, which gives Te = 130·5.

The present investigation was undertaken with the view of ascertaining whether a careful repetition of Berzelius's experiments, made with pure tellurium, would yield a number agreeing with the hitherto adopted atomic weight, or whether it would harmonise with Mendelejeff's classification (*Ann. Chem. Pharm.*, 1871, Supp. Bd., **8**, 133).

According to this classification, we should expect tellurium to have an atomic weight lying between that of iodine = 126·53, and that of antimony = 122, thus taking its place in the same series as sulphur and selenium, the atomic weight which Mendelejeff assigns to it being 125. The experimental results which I have obtained agree closely with those of Berzelius and von Hauer, according to which tellurium has a higher atomic weight than that of iodine, and must, therefore, be placed after this element in Mendelejeff's system.

Preparation of Pure Tellurium.—100 grams of crude tellurium was obtained from Trommsdorff, and a preliminary examination of this showed that it contained copper, bismuth, antimony, tin, &c., as impurities.

The following mode of purification was adopted:—The powdered substance was mixed with three times its weight of dry sodium car-

bonate and three times its weight of sulphur in a porcelain crucible; this was placed inside a fire-clay one and the mass fused in a small furnace. The mass when cold was exhausted with boiling water and filtered from a black insoluble residue; this last contains the sulphides of copper, bismuth, &c.; the deep-yellow filtrate may contain the sulpho-acids of tellurium, selenium, arsenic, tin, and antimony, the tellurium existing as sodium thio-tellurite, Na_2TeS_3. After boiling down, the filtrate was acidified with acetic acid, which precipitates the sulphides of tellurium, tin, &c. The precipitate obtained consisted chiefly of tellurium disulphide, and was nearly black. After filtering it was well washed with water containing sulphuretted hydrogen, and was then brought into a basin and oxidised. The best oxidising agent was found to be pure strong nitric acid, which rapidly dissolved the sulphides, with separation of sulphur. The solution was boiled to dryness, a white mass of tellurium oxide, mixed with sulphur, being left. This was twice treated with strong hydrochloric acid to expel nitric acid; finally an excess of strong hydrochloric acid was added, and, after filtering, a bright-yellow solution was obtained. This was concentrated, put in a flask and warmed, and a solution of sodium sulphite added by degrees, the whole being frequently shaken. In this way a black finely-divided precipitate of tellurium is obtained, any selenium in solution being at the same time precipitated. The precipitate was completely washed, first with dilute hydrochloric acid, and finally with water, and was then dried in an air-bath at 110°. To free this from selenium and sulphur, it was mixed with five times its weight of pure potassium cyanide in a porcelain crucible, this being closed with a lid having a small hole drilled through it to allow of the passage of a tube. Fusion was effected in a small furnace, a current of coal-gas being passed into the crucible throughout the operation and until the crucible was quite cold. The mixture fuses, evolving white fumes to a slight extent, and solidifies on cooling to a dark porous mass. On addition of water this dissolves to a splendid deep claret-coloured solution, which at once deposits some tellurium as a fine powder. The concentrated solution placed in a flask deposits on standing part of the tellurium in the form of long needle-shaped crystals, and a larger portion as a fine amorphous powder. When air has free access, as in a wide-mouthed vessel, or when air is passed through the solution, all the tellurium is deposited in the amorphous form. Both forms are insoluble in hydrochloric acid and in carbon disulphide. The tellurium was finally filtered off, washed completely with water, and dried in an air-bath. In the above processes the sulphur and selenium go into solution as selenio- and thio-cyanates of potassium, the tellurium existing as potassium telluride, the solution of which is decomposed by air with separation of tellurium. The

final purification consisted in distilling the tellurium thus obtained in a current of pure hydrogen obtained by passing the gas generated in the usual way through wash-bottles containing:—(*a*, *b*) silver nitrate; (*c*) caustic soda; (*d*, *e*) boiled sulphuric acid; then over pumice soaked with strong sulphuric acid, and, lastly, over platinum-black heated to redness. All the joints of the apparatus were well paraffined and tied with copper wire, and the whole was arranged so as to give a constant supply of hydrogen for many consecutive hours. The tellurium obtained as described was placed in a porcelain boat, and this in a slightly inclined combustion-tube connected with the hydrogen apparatus. A stream of hydrogen was first passed through the tube for some hours; the tellurium was then gradually heated, and soon fused to a metallic-looking mass, volatilising at a higher temperature in yellow vapours which condensed in the cooler parts of the tube. A small portion is deposited in long needles, the remainder as a metallic mass which solidified on cooling and is crystalline on the surface. A small black residue was left. On redistillation the tellurium left no sensible residue: the distilled tellurium thus obtained easily separates from the tube; it is very bright, has a silver-like lustre, and does not tarnish when kept in a stoppered bottle.

The distilled tellurium used for the final determinations was fused a second time with potassium cyanide in a current of hydrogen; the potassium telluride extracted with water, freed from air as far as possible by boiling, and the tellurium collected in two portions (1) that which precipitated on the filter (marked A), and (2) that which precipitated after the solution had passed through the filter (marked B). Finally, the tellurium obtained from each of these two portions was again distilled in hydrogen. No appreciable difference in the atomic weight was found in the results obtained when using the portion once purified, that twice purified, or either of the portions A and B.

The reagents used were water, nitric acid, and hydrochloric acid.

Pure water was obtained by re-distilling ordinary distilled water from a platinum retort, and condensing in a hard glass vessel. It left no sensible residue on evaporation.

Pure nitric acid was obtained by distilling the commercial acid until free from chlorine; the acid thus obtained was twice re-distilled, and before its final use was again distilled from a platinum retort and condensed in a platinum vessel.

Pure hydrochloric acid was obtained by distilling the strong acid obtained by passing hydrochloric acid gas into water, in a platinum retort connected with a hard glass receiver.

The pure acids on evaporation in contact with air leave a small residue, due to the fixation of foreign matter from the air, this being almost completely volatile at a low red-heat. The residue left on

evaporation was estimated and allowed for when necessary. The final distillations of the reagents were always made just before they were used.

Means of Weighing.—A set of normal weights, by Staudinger, of Giessen, was first carefully calibrated by weighing by vibration. The following table was thus arrived at, one of the 10 gram pieces being taken as normal.

Table of true Relative Weights.

D = denomination of weight. W = true relative weight.

D.	W.	D.	W.
100	100·00064	0·5	0·49997
100′	100·00054	0·2	0·20000
50	50·00024	0·1	0·10000
20	20·00015	0·1′	0·09997
10	10·00000	0·05	0·04998
10′	9·99998	0·02	0·01997
5	5·00004	0·01	0·00999
2	1·99997	0·01′	0·00999
1	1·00004	* 0·01″....	0·01000
1′	0·99999	* 0·01‴ ..	0·01002
1″	1·00001	* 0·01⁗ ..	0·01001

The balance used is by Oertling, and is fitted with a special arrangement for increasing its accuracy. An arrangement of two right angled prisms, into which the pointer screws, is placed on a line with the centre knife edge. By total reflection from these prisms two ivory scales placed on either side of the balance-case are seen through a telescope fitted into the front of the balance case; one of these (A) is divided into 100 divisions, the other (B) has a single mark across its centre. The prisms and scales are so arranged that when the pointer is at the centre division of the ordinary scale (C), the mark on scale B is continuous with the centre division of scale A, and as the pointer (hence the prisms) moves, the mark on scale B moves along the scale A in such way that one division of the ordinary scale corresponds to five divisions of scale A. Since it is easy to read accurately to half a division of scale A, it is thereby possible to read directly and without error to tenths of an ordinary scale division.

The following numbers indicate the sensibility of the balance: δ = weight in milligrams, corresponding to one division of the ordinary scale, *i.e.*, to five of the scale A.

* Riders.

Load in grams.	δ.
0	0·066
10	0·066
30	0·072
50	0·073
75	0·084
100	0·096

The method of weighing used was that of vibrations. The position of rest with no load on the pans was first observed; the object to be weighed is then slightly more than balanced, and the position of rest again taken; half milligram weight is then removed and the resting point taken, and finally the position of rest with nothing on the pans is again noted. In this manner the sensibility of the balance is ascertained at each weighing, and it becomes possible to weigh with very great accuracy. Generally three swings of the pointer were observed, the first one (or two) being neglected as not sufficiently regular.

The objects to be weighed (unless hygroscopic) were always left in the balance case some time before weighing, and until they became quite constant in weight.

Experiments on the Oxidation of Tellurium with Nitric Acid.

Berzelius showed that by using nitric acid of sp. gr. 1·25 containing 40 per cent. HNO_3, tellurium is dissolved, with formation of the dioxide which separates out; and that only a very small quantity of the trioxide is formed at the same time.

Nitric acid of the above strength dissolves tellurium rapidly in the cold; nitric acid of sp. gr. 1·47, containing 83·5 per cent. HNO_3, has at the ordinary temperature no action, but on warming on a water-bath the action proceeds slowly up to a certain point, when it becomes rapid. The amount of $TeO_3.3H_2O$ formed, varies according to the strength of acid used, as will be seen by the following table:—

Experiment.	Acid, sp. gr. 1·47.	Water.	Percentage increase at 100—110°.
I.....	18·5 c.c.	4 c.c.	48·47
II.....	excess „	0 „	46·27
III.....	6 „	6 „	25·15
IV	5 „	0 „	49·98
V	2 „	2 „	25·22

The percentage increase for $TeO_2 = 24·9$; for $TeO_3 = 37·5$; for $TeO_3.3H_2O = 79·7$.

When using nitric acid of sp. gr. 1·25, the amount of tellurium taken influences the reaction. With small quantities all the tellurium

is dissolved; if larger quantities be used, the action is not complete; the tellurium dioxide formed is nearly insoluble in nitric acid and in water, and appears to coat over the tellurium, and thus protect it from further action. Thus the following numbers were obtained:—

Experiment.	Weight of Te taken.	Weight of unoxidised portion.
I.....	8·2548 grams.	0·88 gram.
II	4·8067 „	0·0285 „
III	2·6507 „	0·0005 „

When telluric acid, $TeO_3.3H_3O$, is heated to 180° it loses 2 molecules of water, and the H_2TeO_4 left loses on further heating first the remaining water and then one atom of oxygen. Between 180° and 350° there is a gradual loss in weight, no distinct temperature being noted at which the trioxide begins to lose oxygen and become dioxide. To completely convert all TeO_3 into TeO_2 it is necessary to heat it cautiously in a covered crucible over the flame until the oxide just begins to fuse round the edges; the mass then consists of pure tellurium dioxide, and no loss by volatilisation occurs.

The method employed for converting a given weight of tellurium into tellurium dioxide was as follows: Pure tellurium was finely powdered in an agate mortar, and weighed in a platinum crucible, after drying at 100—105°. Strong nitric acid, or this mixed with water, was then very gradually added by means of a pipette, a watch-glass being placed over the crucible to prevent loss by spirting. After the action had ceased, the acid was evaporated to dryness on a water-bath, the watch-glass being left on until it had been washed perfectly clean by the acid which condensed and ran back, as shown by its drying in the air without the least residue being left on it. 1 c.c. of acid was finally added, and the whole evaporated again to dryness. The crucible was then slowly heated in an air-bath up to 350°, there being a gradual loss of weight corresponding with the decomposition of $TeO_3.3H_2O$ by heat. Thus the following results were obtained, giving the increase of weight observed on 100 parts of tellurium:—

	Temperature.	I.	II.
Percentage increase at	100°.....	48·5 per cent.	49·9 per cent.
	180	35·6 „	36·2 „
	230	31·6 „	32·9 „
	350	25·3 „	26·5 „

In the first experiment distinct crystals of $TeO_3.3H_2O$ were obtained, the gradual conversion of which into dioxide was plainly seen. Finally the oxide was cautiously heated over a lamp in such a way that no loss through volatilisation occurred, until the weight became

constant. The tellurium dioxide obtained is not sensibly hygroscopic.

The following results were obtained in this way: (O = 15·96).

Experiment.	Te taken.	TeO_2 found.	Percentage of Te.	Atomic weight.	Error.
I.....	2·21613	2·77612	79·83	126·31	−1·49
II.....	1·45313	1·81542	80·04	128·03	+0·23
III.....	2·67093	3·33838	80·01	127·73	−0·07
IV.....	4·77828	5·95748	80·21	129·34	+1·54
V.....	2·65029	3·31331	79·98	127·59	−0·21

Mean atomic weight = 127·80.

In No. I the oxide was only heated to 350°, so that the last traces of TeO_3 were not decomposed: it was afterwards fused, during which there was slight loss, the atomic weight calculated from the weight of the oxide after fusion being 129·2. In Experiments IV and V, oxidation was not complete; the unoxidised tellurium was estimated by dissolving out the dioxide with hydrochloric acid, washing by decantation, and weighing the residue dried at 105°. This weight was deducted from the weight of oxide found, and from the weight of tellurium taken, and the atomic weight deduced from the corrected numbers, which are those given above. In No. IV the insoluble portion weighed 0·02846 gram, in No. V 0·00044 gram; in this last case the error caused by neglecting this altogether affects the atomic weight in the second decimal place only.

The mean of these five experiments gives the number 127·80, with a probable error of 0·32, whilst that of II, III, and V, which are the most trustworthy, is 127·78 with a probable error of 0·09.

Experiments I, II, and III, were made with tellurium once purified, IV and V with that twice purified. The occurrence in some experiments of a small unoxidised portion seemed to point to impurities: some pure tellurium was, therefore, distilled in hydrogen until about one half had been carried over; the operation was then stopped, and the more and the less volatile portions collected and acted on with nitric acid. No sensible difference was found in the two cases.

Portions of pure tellurium, and of that which remained unoxidised, were also examined with the spectroscope, but no difference between the two spectra could be detected.

Experiments on the Oxidation of Tellurium by Aqua-regia.

To obviate the error occasioned by the possible incomplete oxidation when nitric acid alone acts on tellurium, aqua-regia was next employed as oxidising agent. This necessitated the use of porcelain

in place of platinum vessels, and it was found that the former always underwent a slight loss of weight, but this never amounted to as much as a tenth of a milligram in the course of a single experiment.

By the action of aqua-regia on tellurium a mixture of TeO_2 and $TeO_3.3H_2O$ is formed. As before, a weighed quantity of tellurium was taken and treated exactly as above described, with the exception that the nitric acid was replaced by aqua-regia. The tellurium dissolves quickly, aqua-regia being added until no further action goes on; on evaporation to dryness a white mass was left. Nitric acid alone was next added; this again evaporated to dryness; and the addition of acid and subsequent evaporation once more repeated.

The percentage increase at 140° was found to be as follows:—

I.	II.	III.	IV.
42·6	47·3	37·4	36·2 per cent.

On raising the mass to a higher temperature, nitrous fumes are evolved, and on gradual heating in the air-bath and finally cautiously heating over a flame, pure tellurium dioxide is left. The following numbers were thus obtained:—

Experiment.	Te taken.	TeO_2 found.	Percentage of Te.	Atomic weight.	Error.
I.....	2·85011	3·56158	80·02	127·88	−0·03
II.....	3·09673	3·86897	80·04	128·00	+0·09
III.....	5·09365	6·36612	80·01	127·77	−0·14
IV.....	3·26604	4·08064	80·04	127·98	+0·07

The mean atomic weight is, therefore, 127·907, with a probable error of 0·053.

Experiments I, II, and III, were made in a porcelain crucible; No. IV in a small glass flask, placed with the neck in a nearly horizontal position. In this way any possible loss by spirting, when the acid acts on the tellurium, was avoided, and the heating could also be carried on with greater ease and less fear of loss than before.

I and II were made with the same sample of tellurium, after distilling in hydrogen and collecting in two portions. I was made with the more volatile portion; II with the less volatile portion. All these four experiments were made with twice purified tellurium, I and II with that marked A; III and IV with that marked B.

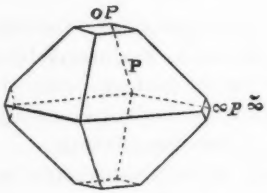
Analysis of Bromide of Tellurium and Potassium.

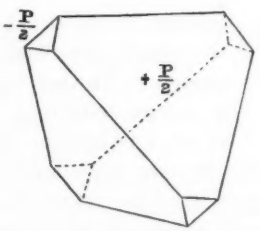
As a check upon the atomic weight determined as described, I have analysed the compound K_2TeBr_6 in the manner that von Hauer describes. The crystallised salt was prepared according to his method as follows:—Equivalent quantities of tellurium and pure potas-

sium bromide were placed in a flask, and water added until the potassium bromide dissolved. Pure bromine was then gradually run in, and the flask shaken frequently. The bromine disappears, as does the tellurium, slowly, and an orange-yellow liquid is formed. A small yellow deposit forms at the same time. The liquid is decanted from this, and the excess of bromine evaporated off on a water-bath. The concentrated hot solution deposits on cooling crystals of the double salt, which crystallises exceedingly well. To recrystallise the salt, it was dried and then dissolved in a small quantity of hot water; tellurous acid then separates out at first but redissolves, unless there be an excess of water, when it remains permanent. Mr. Baker has kindly made the following measurements and determination of the crystalline form for me:—

Rhombic.—Forms observed P.0P.∞P$\breve{\infty}$. Type pyramidal; or $+\frac{P}{2}, -\frac{P}{2}$, the former often greatly predominating. Faces of P perfectly smooth and with a brilliant lustre; those of the basal plane and brachypinacoïd uneven. Axes $\dot{a} : \bar{b} : \dot{c} = 1{\cdot}0000 : 1{\cdot}4901 : 1{\cdot}3658$.

		Calculated from above ratios.
$\bar{1}11 : \bar{1}\bar{1}1$	= 123° 9·9′	= 123° 9·1′
$111 : 1\bar{1}1$	= 123 10·6	
$\bar{1}11 : 11\bar{1}$	= 56 52·0	= 56 50·9
$\bar{1}11 : 111$	= 89 33·8	= 89 36·5
$1\bar{1}1 : \bar{1}\bar{1}1$	= 89 37·3	
$1\bar{1}1 : 11\bar{1}$	= 90 24·4	= 90 23·5
$\bar{1}11 : 1\bar{1}1$	= 62 34·5	= 62 34·5





On heating to 120°, the salt loses water and becomes orange-coloured; it remains quite constant in weight between 120° and 160°.

For analysis a weighed quantity of the anhydrous salt was dissolved in dilute nitric acid (strong nitric acid liberates bromine) and precipitated with a solution of silver nitrate. The resulting silver bromide was washed many times with dilute nitric acid, and finally with water; it was then dried and weighed in the usual way.

The following results were thus obtained (Ag = 107·66; Br = 79·75; K = 39·04).

Experiment.	K_2TeBr_6 taken.	AgBr found.	Percentage of Br.	Atomic weight.	Error.
I.....	1·70673	2·80499	69·93	127·61	+0·78
II.....	1·75225	2·88072	69·96	127·40	+0·57
III.....	2·06938	3·40739	70·07	126·33	−0·50
IV.....	3·29794	5·43228	70·09	126·07	−0·76
V.....	2·46545	4·05742	70·03	126·72	−0·11

The mean of these determinations gives Te = 126·83, with a probable error of 0·198. This is somewhat lower than von Hauer's mean number obtained in a similar way, and also lower than the number obtained by the oxidation method. Von Hauer found, as a mean of five experiments, 69·92 per cent. of bromine, the mean percentage which I obtain being 70·02.

Experiments I and IV were made with one sample, twice crystallised; Nos. II, III, and V, with another sample three times crystallised. In all cases only the distinct crystals were selected and used for analysis.

The conclusions which I draw from the three series of experiments is that the atomic weight of tellurium does not lie between those of iodine and antimony, but is greater than that of the former element, which must, therefore, precede tellurium in Mendelejeff's classification.

LXIII.—*Note on the Magnesium Vanadates.*

By R. Sugiura and H. Baker, Students in the Chemical Laboratories of The Owens College, Manchester.

Von Hauer described in 1860 (*J. pr. Chem.*, **80**, 329) a magnesium divanadate having the formula $MgO.2VO_3 + 8HO$ [V = 68·6, Mg = 12, O = 8], obtained by mixing solutions of magnesium sulphate and ammonium divanadate, and crystallising the sparingly soluble salt from hot water. On account of its slight solubility, it is difficult to obtain in large crystals, and furthermore its solution is somewhat readily decomposed on heating, with separation of vanadic acid. The description of this salt is concluded with the words:—"Mit der genaueren Untersuchung dieser und mehrere anderer dreifachvanadinsaurer Salze bin ich noch nicht zum Abschlusse gelangt, und behalte mir die Mittheilung für später vor." However, in none of the successive numbers of the Journal have we been able to find such a communication.

By boiling "magnesia alba" with water and amorphous vanadic acid, carbonic acid is rapidly evolved, and on filtering off the excess of magnesia alba, a colourless liquid is obtained. On evaporating this liquid a white mass is left, not sensibly crystalline, and giving discrepant results on analysis, whence it appears to be merely a mixture of magnesia and a neutral vanadate. If, on the other hand, acetic acid be added in excess, the liquid becomes deep red-brown, and on spontaneous evaporation it readily deposits crystals, leaving a syrupy solution of magnesium acetate. Two lots of crystals were thus obtained, one of a deep yellowish-brown, or almost black colour; and the other of a bright bichromate-red, both transparent.

I. *Brown Salt.*—A weighed portion of the crystals dissolved in water was precipitated with lead acetate. The washed precipitate was dissolved in nitric acid, and the solution precipitated with sulphuric acid; the filtrate after evaporation to a syrup was diluted with a very little water and the small quantity of lead sulphate filtered off; lastly this filtrate when evaporated and ignited left vanadic oxide. The filtrate from the lead vanadate, after precipitation with sulphuretted hydrogen, was concentrated, and the magnesia precipitated as usual with ammonium phosphate.

0·4025 substance lost 0·1315 on ignition; 0·3565 gave 0·0770 $Mg_2P_2O_7$; 0·3015 gave 0·1788 V_2O_5, and 0·0692 $Mg_2P_2O_7$. Another preparation gave 60·02 p. c. V_2O_5; 7·66 p. c. MgO; and 33·00 p. c. H_2O.

	$3MgO.5V_2O_5\,28H_2O$.	Found.			Mean.
V_2O_5.....	59·40	—	59·30	60·02	59·66
MgO	7·82	7·78	8·27	7·66	7·90
H_2O.....	32·78	32·73	—	33·00	32·86
	100·00				100·42

This salt forms crystals belonging to the triclinic system; the type is always short prismatic, through the predominance of the vertical prisms and pinacoïds, of which the brachypinacoïd is most developed; they are terminated by the basal planes and brachypinacoïds. The forms observed are $\infty P\breve{\infty}$. $\infty P'$. $\infty P\bar{2}'$. $\infty P\bar{2}$. $\infty P\bar{\infty}$. $\frac{1}{2}P\breve{\infty}'$. $\frac{1}{2}P\breve{\infty}$. $+P\bar{\infty}$. $+P'$ (Fig. 1). The prismatic faces, with the exception of the brachypinacoïd, are often vertically striated, especially $\infty P\bar{2}'$ and $\infty P\bar{\infty}$; the basal plane is nearly always deeply striated, parallel to the brachy-axis; the faces of $+P'$ are also striated parallel to their combination-edge with the brachypinacoïd. The faces are always very lustrous, but do not generally give sharp images by reflection. The elements are:— $\breve{a} : \bar{b} : \dot{c} = 1{\cdot}000 : 1{\cdot}003 : 1{\cdot}012$; $\alpha = 89° 24'$; $\beta = 104° 20'$; $\gamma = 82° 22'$; and the interfacial angles are:—

	Calculated.	Found.	No. of observations.
$\infty P\bar{\infty} : \infty P\bar{\infty} = (100) : (010) =$	81° 58′	81° 41′	3
$\infty P\bar{\infty} : \infty P' = (100) : (110) =$	132 8	132 4	1
$\infty P\bar{\infty} : \infty P\bar{2}' = (100) : (210) =$	152 52	151 50	2
$\infty P\bar{\infty} : \infty P\bar{2} = (100) : (2\bar{1}0) =$	155 51	156 34	2
$\infty P\bar{\infty} : \infty P' = (010) : (110) =$	129 50	129 54	4
$\infty P\bar{\infty} : \infty P\bar{2}' = (010) : (210) =$	109 6	109 6	1
$\infty P\bar{\infty} : \infty P\bar{2} = (010) : (2\bar{1}0) =$	122 11	121 51	4
$\infty P' : \infty P\bar{2}' = (110) : (210) =$	159 16	159 52	2
$\infty P\bar{\infty} : \frac{1}{2}P\bar{\infty}' = (010) : (012) =$	114 10	114 35	5
$\infty P\bar{\infty} : 0P = (010) : (001) =$	87 25	87 3	3
$(\infty P\bar{\infty}) : \frac{1}{2}P\bar{\infty} = (0\bar{1}0) : (0\bar{1}2) =$	118 18	118 4	5
$0P : \frac{1}{2}P\bar{\infty}' = (001) : (012) =$	153 15	153 23	5
$0P : \frac{1}{2}P\bar{\infty} = (001) : (0\bar{1}2) =$	154 17	154 32	4
$\frac{1}{2}P\bar{\infty} : \frac{1}{2}P\bar{\infty}' = (0\bar{1}2) : (012) =$	127 32	127 39	2
$\infty P\bar{\infty} : 0P = (100) : (001) =$	104 33	104 29	4
$\infty P\bar{\infty} : +P\bar{\infty} = (100) : (10\bar{1}) =$	128 51	128 52	2
$(0P) : +P\bar{\infty} = (00\bar{1}) : (10\bar{1}) =$	126 56	126 40	2
$(\infty P\bar{\infty}) : +P\bar{\infty} = (0\bar{1}0) : (10\bar{1}) =$	94 32	95 2	6
$+P\bar{\infty} : +P' = (10\bar{1}) : (11\bar{1}) =$	139 41	139 38	3
$\infty P\bar{\infty} : +P' = (010) : (11\bar{1}) =$	125 47	125 30	3
$\infty P' : +P' = (110) : (11\bar{1}) =$	139 32	139 29	2
$\frac{1}{2}P\bar{\infty}' : \infty P' = (012) : (110) =$	115 50	115 50	4
$\frac{1}{2}P\bar{\infty} : (+P\bar{\infty}) = (012) : (\bar{1}01) =$	125 46	125 33	1

The crystals are not uncommonly twinned in such a manner that the brachydomes of the second crystal fall in the same zone as the prismatic faces of the first, and conversely, and the brachypinacoïds of the two individuals are parallel: hence the twin axis is the bisectrix of the axial angle β (Fig. 2).

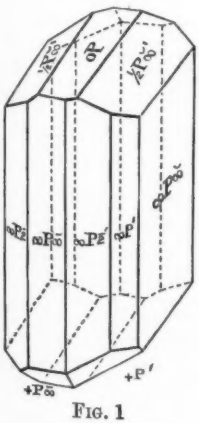


FIG. 1

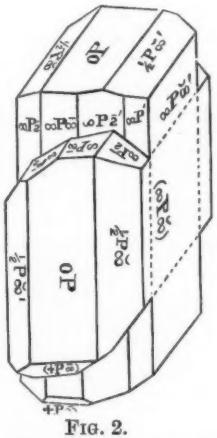


FIG. 2.

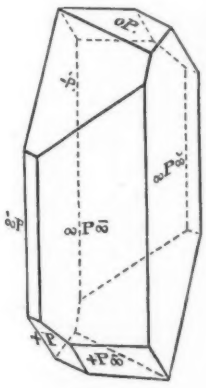


FIG. 3.

II. *Red Salt.*—The analyses of this salt gave the following results:—

0·2880 gram lost 0·0942 on ignition; 0·3155 substance gave 0·1902 V_2O_5 = 59·73 V_2O_5 p. c.; this was fused with acid potassium sulphate, the fused mass dissolved in dilute sulphuric acid, and the solution after reduction with sodium sulphite and boiling was reoxidised with potassium permanganate solution (1 c.c. = 0·00611 V_2O_5), 30·75 c.c. were used, giving p. c. V_2O_5 = 59·55; mean, 59·64. 0·3375 gram substance lost 0·1091 gram on ignition, the residue fused with acid potassium sulphate and treated as above required 33·3 c.c. potassium permanganate solution.

$3MgO.5V_2O_5.28H_2O$.		Found.		Mean.
V_2O_5.....	59·40	59·64	60·30	59·97
MgO	7·82	—	—	7·52 (by diff.)
H_2O.....	32·78	32·73	32·29	32·51

This red salt has, therefore, the same composition as the brown salt, and, like the latter, it also belongs to the triclinic system, but no relation between the two sets of forms is evident; the sp. gr. of the "brown salt" at 18° C., taken in benzene, was found to be 2·199, and that of the "red salt" 2·167; both forms are perfectly stable in the air.

The type of the red crystals is short prismatic, through predominance of the vertical pinacoïds. Faces very lustrous, and, excepting the brachypinacoïd, which is often bent, very well formed; none of the faces are striated. The occurring forms are $\infty P\breve{\infty}.\infty P\bar{\infty}$. $-P.\infty P$. $+P$. $0P$. $+P\bar{\infty}$ (Fig. 3). $\breve{a} : \bar{b} : \dot{c} = 1{\cdot}000 : 1{\cdot}261 : 0{\cdot}8525$, and the inclinations of the axes in the upper right octant are $\alpha = 93° 35'$; $\beta = 101° 30'$; $\gamma = 166° 55'$; the interfacial angles are:—

	Calculated.	Found.	No. of observations.
$0P : \infty P\bar{\infty} = (001) : (100)$	$= 103° 10'$	$103° 10'$	1
$+P\bar{\infty} : \infty P\bar{\infty} = (10\bar{1}) : (100)$	$= 124\ 11$	$124\ 7$	5
$+P\bar{\infty} : (0P) = (10\bar{1}) : (00\bar{1})$	$= 132\ 39$	$132\ 38$	1
$\infty P\bar{\infty} : \infty P\breve{\infty} = (100) : (010)$	$= 108\ 4$	$108\ 13$	5
$\infty P : (\infty P\breve{\infty}) = (1\bar{1}0) : (010)$	$= 116\ 14$	$116\ 16$	3
$\infty P : \infty P\bar{\infty} = (1\bar{1}0) : (100)$	$= 135\ 42$	$136\ 5$	2
$\infty P : -P = (1\bar{1}0) : (1\bar{1}1)$	$= 136\ 58$	$136\ 58$	3
$-P : 0P = (1\bar{1}1) : (001)$	$= 139\ 58$	$139\ 54$	1
$+P : 0P = (1\bar{1}\bar{1}) : (00\bar{1})$	$= 133\ 28$	$133\ 3$	2
$-P : (+P) = (1\bar{1}1) : (\bar{1}11)$	$= 93\ 26$	$93\ 24$	2
$+P\bar{\infty} : \infty P\breve{\infty} = (10\bar{1}) : (010)$	$= 97\ 11$	$97\ 7$	3
$+P\bar{\infty} : +P = (10\bar{1}) : (1\bar{1}\bar{1})$	$= 147\ 47$	$147\ 44$	2
$P : (+P\bar{\infty}) = (1\bar{1}1) : (10\bar{1})$	$= 100\ 29$	$100\ 28$	1
$(\infty P\breve{\infty}) : +P = (0\bar{1}0) : (1\bar{1}\bar{1})$	$= 101\ 26$	$101\ 4$	2
$\infty P\bar{\infty} : +P = (100) : (1\bar{1}\bar{1})$	$= 128\ 20$	$128\ 20$	2
$\infty P\bar{\infty} : -P = (100) : (1\bar{1}1)$	$= 110\ 16$	$110\ 6$	1

These observations show that the salt $3MgO.5V_2O_5.28H_2O$ is dimorphous; no other corresponding vanadate appears to be known.

LXXIV.—*On Mauveine and Allied Colouring Matters.*

By W. H. Perkin, F.R.S.

In 1864 I gave an account of some experiments I had made on the crystallised colouring matter which had been obtained from the commercial mauve dye or aniline purple (*Proc. R. Soc.*, **12**, 713). I then stated that it contained an organic base having the formula $C_{27}H_{24}N_4$. Since then I have at various times made experiments on this product, and now beg to lay before the Society the principal results I have obtained up to the present time.

When the mauve dye was first prepared on the large scale, aniline made from what is now commercially known as 90 per cent. benzole was employed. It was soon found, however, that by using an aniline containing much larger quantities of toluidine, a colouring matter giving redder shades of purple was produced.* By taking advantage of this, two different products were manufactured, namely, a blue shade of mauve prepared from aniline, containing but little toluidine, and a red shade from an aniline containing large quantities of toluidine. The colouring matter was likewise prepared in two qualities, one being made by precipitating the aqueous solution of the crude colouring matter with sodic hydrate, and a second and purer quality by precipitating it with dilute sulphuric acid. It was noticed that the colouring matter precipitated by sulphuric acid had a satiny aspect, and was evidently crystalline, and this was especially the case with the product obtained from aniline containing considerable quantities of toluidine.

On dissolving this crystalline colouring matter in alcohol, and adding a little sulphuric acid, crystals were deposited, which when washed with alcohol, possessed a green metallic reflection. These consisted of what we now know as the sulphate of mauveine. As this salt is difficultly soluble in alcohol, and unsuitable for the dyer, it was boiled in alcohol with potassic acetate, and thus converted into the soluble acetate of mauveine; alcoholic sodic hydrate was then added in excess, and water added, which caused the mauveine to be entirely precipitated. This was collected, well washed, and dried. This mauveine was then dissolved in boiling alcohol acidulated with acetic acid, rapidly filtered, and allowed to stand to crystallise.

When manufacturing this product, it was always found best to use

* The use of toluidine and other homologues of aniline was claimed in the original patent. No. 1984, Aug. 26, 1856.

colouring matter made from aniline containing large quantities of toluidine, otherwise the crop of crystals was very small, most of the colouring matter remaining in solution. An account of the colouring matter found in the mother-liquors in the preparation of crystalline mauveine will be found described further on in this paper.

After the publication of my paper on "Mauve or Aniline Purple," I was induced to modify the formula of mauveine, and to regard it as containing C_{26} instead of C_{27}. This alteration would only require a difference of ·6 per cent. less of carbon, and as my combustions had been made with lead chromate, it was thought that possibly some oxides of nitrogen might have escaped reduction by the copper used. A few numbers were also obtained which seemed to favour this view.

However, a number of careful experiments have since been made, and gave results which I think conclusively settle this point.

The following are combustions of various specimens of the hydrochloride of mauveine dried at 150° C., and burnt in a boat, oxide of copper and metallic copper being used in the combustion tube:—

I. ·227 gram of substance gave
25·88 c.c. of nitrogen at 20° C. and 772·5 mm.

II. ·286 gram of substance gave
·7705 „ of CO_2, and
·143 „ of OH_2.

III. ·276 „ of substance gave
·741 „ of CO_2, and
·14 „ of OH_2.

IV. ·293 „ of substance gave
·791 „ of CO_2, and
·146 „ of OH_2.

V. ·287 „ of substance gave
·771 „ of CO_2, and
·145 „ of OH_2.

VI. ·2345 „ of substance gave
·6310 „ of CO_2, and
·125 „ of OH_2.

VII. ·243 „ of substance gave
·6535 „ of CO_3, and
·127 „ of OH_2.

VIII. ·2705 „ of substance gave
·725 „ of CO_2, and
·139 „ of OH_2.

	Theory for $C_{26}H_{24}N_4$.	Theory for $C_{27}H_{24}N_4$.
Carbon	72·81	73·55
Hydrogen	5·83	5·67
Nitrogen	13·06	12·73

	Experiment.			
	I.	II.	III.	IV.
Carbon....	—	73·47	73·22	73·6
Hydrogen .	—	5·55	5·63	5·54
Nitrogen ..	13·15	—	—	—

	Experiment.				
	V.	VI.	VII.	VIII.	Average.
Carbon.....	73·26	73·39	73·34	73·09	73·34
Hydrogen....	5·61	5·49	5·80	5·70	5·61
Nitrogen	—	—	—	—	13·15

Experiments were also made to find what quantity of hydrochloric acid a known weight of mauveine would combine with.

The following results were obtained:—

I. 3·0362 gram of mauveine combined with
·2737 „ of HCl.

II. 3·5869 „ of mauveine combined with
·3205 „ of HCl.

The molecular weight of mauveine calculated from these experiments is	406·7
The formula $C_{27}H_{24}N_4$ requires.....	404·0
„ $C_{26}H_{24}N_4$ „	392·0

The following fresh analyses of the platinum salt were also made:—

I. ·550 gram of substance gave
·088 „ of platinum.

II. ·465 „ of substance gave
·9085 „ of CO_2, and
·1755 „ of OH_2.

III. ·376 „ of substance gave
·730 „ of CO_2, and
·144 „ of OH_2.

	Theory for $(C_{26}H_{24}N_4)_2H_2PtCl_6$.	Theory for $(C_{27}H_{24}N_4)_2H_2PtCl_6$.
Carbon	52·15	53·09
Hydrogen	4·34	4·09
Platinum	16·5	16·16

	Experiment.		
	I.	II.	III.
Carbon	—	53·28	52·95
Hydrogen	—	4·19	4·25
Platinum	16·0	—	—

These results therefore confirm the original formula, $C_{27}H_{21}N_4$.

The platinum salt of mauveine when heated with water to between 120° and 150° C., gives up hydrochloric acid and hydrochloride of mauveine, which is easily removed by alcohol. From platinum determinations in the residue it appears probable that the decomposition takes place as follows:—

$$(C_{27}H_{24}N_4)_2H_2PtCl_6 = C_{27}H_{24}N_4PtCl_4 + C_{27}H_{24}N_4,HCl + HCl.$$

It is well known that mauveine yields different coloured solutions when mixed with acids in various states of concentration: thus, with dilute acids the ordinary purple solutions are obtained, if more concentrated blue solutions, and when very concentrated, as with ordinary sulphuric acid, dirty green solutions.

As it was believed that these colours indicated the existence of different salts, as in the case of rosaniline, attempts were made to prepare one of them.

On adding concentrated hydrochloric acid to a strong alcoholic solution of the acetate of mauveine until it becomes thoroughly blue, a quantity of a crystalline salt possessing a coppery lustre soon separates. This, after being pressed between linen, is found to be blue by transmitted light, but when washed with water or a little alcohol changes to purple, being converted into the ordinary hydrochloride. This salt is believed to be an acid hydrochloride, having the formula—

$$C_{27}H_{24}N_4.2HCl.$$

To prove this an attempt was made to produce the corresponding platinum salt. For this purpose, a somewhat dilute solution of acetate of mauveine was treated with an excess of concentrated hydrochloric acid, so that crystals might not separate; to this a solution of platinic chloride in concentrated hydrochloric acid was added. The dark blue precipitate which formed immediately was collected, washed with concentrated hydrochloric acid, pressed, and then dried by being placed in a bell-jar over caustic lime. It had a coppery aspect. When dry it was powdered and heated in the water-oven until constant. It gave on analysis 23·2 per cent. of platinum, the formula $C_{27}H_{24}N_4,H_2PtCl_6$ requiring 24·18 per cent. This result, although not very good, is perhaps as near as could be expected. This blue platinum salt, when washed with water, loses platinic chloride and hydrochloric acid.

Mauveine and Sulphuric Acid.

Mauveine may be heated with ordinary concentrated sulphuric acid without undergoing any change, but if fuming acid containing 50 per cent. SO_3 be used, on heating the mixture the mauveine is converted into a soluble sulpho-acid, forming blue-violet salts.

Action of Heat on Mauveine.

I have on a previous occasion mentioned that mauveine, when heated with aniline, produces a blue colouring matter which was believed to be a phenylic derivative of that base.

On heating acetate of mauveine with aniline the reaction takes place pretty readily, but no ammonia is given off. Numerous quantities of this blue product have been prepared and analysed, but no numbers have been obtained corresponding with those required by a phenylated mauveine or a compound of mauveine and aniline.

From experiments I have lately made I am induced to think that aniline plays no part in this reaction, as I find that pure mauveine, if carefully fused, yields a blue product apparently identical with that obtained when aniline is heated with it.

I am still experimenting in this direction, and hope to obtain a clearer insight into this reaction and the nature of the colouring matter produced.

Mauveine and Ethylic Iodide.

Ethylic iodide acts rapidly upon mauveine at 100° C., with formation of hydriodide of mauveine and an ethylated derivative. The effect of ethylation, however, is quite different in this instance from that of rosaniline, so far as its influence on the colour of the compound is concerned, as in that case it becomes bluer, whilst in this it becomes redder.

Ethylated mauveine was manufactured commercially and known as "Dahlia." Its colour is between that of a salt of mauveine and rosaniline. As a colouring matter it resists the action of light to about the same extent as mauveine, and can be applied to dyeing and calico-printing in the same manner.

In manufacturing this product, mauveine, prepared from the crystallised acetate, was heated for three or four hours with alcohol and ethylic iodide. It was then allowed to cool thoroughly, and afterwards filtered off from the difficultly soluble hydriodide of mauveine which had been formed. Any free ethylic iodide was then distilled off, and the product diluted with alcohol until of a suitable strength for the consumer.

Sometimes magnificent crystals were deposited from strong solutions of the ethylated mauveine. They were oblique and possessed a golden-green metallic lustre. Their alcoholic solution was of nearly the same colour as the mother-liquor from which they were deposited. When these were formed in any quantity in an operation there was generally a good deal of an almost insoluble blackish-blue product containing iodine found associated with the hydriodate of mauveine.

A great many analyses of these beautiful crystals were made, but the composition of different preparations varied, none of them giving numbers agreeing with the hydriodide of an ethyl-mauveine, the carbon always coming too low. At last it was found that they contained, besides hydriodic acid, combined iodine. This was first discovered on the examination of a specimen which gave exceptionally low carbon determinations, and it was found, on treating it with an alcoholic solution of silver tartrate, that only part of the iodine was precipitated. This specimen was recrystallised from alcohol six times, and gave numbers which are not very far from those required by the formula—

$$C_{27}H_{23}(C_2H_5)N_4.HI.I_2.$$

	Theory.	Experiment. I.	II.	III.
C	42·75	43·85	43·77	43·85
H	3·56	4·34	4·09	4·15

I have not been able to produce this substance at will, nor do I know the circumstances which most favour its formation. The other specimens of these crystals examined were apparently a mixture of this product and hydriodide of ethyl-mauveine.

To obtain compounds of ethyl-mauveine in a state of tolerable purity the following method was employed.

The crude alcoholic solution of the hydriodide, after being filtered from the hydriodide of mauveine, and heated to remove any excess of ethylic iodide, was diluted with alcohol, and mixed with alcoholic sodic hydrate. It was then gradually added to water to precipitate the colouring matter, which was then collected on a filter and washed. When the saline matter had been removed, and the colouring matter began to dissolve, warm water was used, and the coloured filtrate collected, the washing being continued until it became weak in colour. (From experiments I have lately made, I believe it would be better to boil the washed precipitated colouring matter in water, and then filter off the strongly coloured fluid.) The solution thus obtained was then saturated with sodium chloride, and after standing the colouring matter which had precipitated collected on a filter, and washed until it began to be dissolved. It was then redissolved in a

little boiling water, filtered, and allowed to stand, when it separated out as a crystalline precipitate of a brownish-red colour. This product is the hydrochloride of ethyl-mauveine, and gave the following numbers on analysis:—

I. ·277 gram of substance gave
·749 „ of CO_2 and
·157 „ of OH_2.

II. ·239 „ of substance gave
23·37 c.c. of N at 17° and 764 mm.

III. ·207 gram of substance gave
20·75 c.c. of N at 16° and 774 mm.

		Experiment.		
Theory for $C_{27}H_{23}(C_2H_5)N_4HCl$.		I.	II.	III.
Carbon	74·27	73·74	—	—
Hydrogen	6·19	6·37	—	—
Nitrogen	11·95	—	11·82	11·90

The hydrochloride of ethyl-mauveine is very soluble in alcohol, forming a beautifully clear red-purple solution, which cuts off the green and most of the yellow from the spectrum, as in the case of a salt of mauveine. It is also moderately soluble in water; from this solution potassic hydrate separates the colouring matter as a purple-brown powder. Silver oxide also removes the colouring matter as a precipitate, silver chloride being formed at the same time.

Alcoholic potassic hydrate added to an alcoholic solution of the hydrochloride of ethyl-mauveine has but little influence upon its colour. Silver oxide renders it a trifle bluer in shade.

It dissolves in concentrated sulphuric acid, forming a dirty yellowish-green solution, changing to blue, and then to purple as it is diluted. With concentrated hydrochloric acid it forms a beautiful blue solution.

Platinum Salt.—An alcoholic solution of the hydrochloride of ethyl-mauveine, when mixed with platinic chloride also in alcoholic solution, gives a crystalline precipitate with a beautiful golden-green metallic reflection. When viewed under the microscope, this is seen to consist of oblique crystals, which appear like golden spangles by reflected light. This compound is only slightly soluble in alcohol. On analysis it gave the following numbers:—

I. ·491 gram of substance gave
·07425 „ of platinum.

II. ·471 „ of substance gave
·0710 „ of platinum.

III. ·4902 gram of substance gave
·0757 „ of platinum.

IV. ·3927 „ of substance gave
·0607 „ of platinum.

V. ·408 „ of substance gave
·0613 „ of platinum.

VI. ·2756 „ of substance gave
·0430 „ of platinum.

VII. ·2905 „ of substance gave
·5825 „ of CO_2 and
·1314 „ of OH_2.

VIII. ·3067 „ of substance gave
·6144 „ of CO_2 and
·1377 „ of OH_2.

IX. ·4324 „ of substance gave
·0670 „ of platinum.

X. ·3166 „ of substance gave
·6313 „ of CO_2 and
·1438 „ of OH_2.

XI. ·4344 „ of substance gave
·0657 „ of platinum.

XII. ·1710 „ of substance gave
·3440 „ of CO_2 and
·0768 „ of OH_2.

	Theory for $2[C_{27}H_{23}(C_2H_5)N_4].H_2PtCl_6$.	Experiment. I.	II.	III.	IV.
Carbon	54·52	—	—	—	—
Hydrogen ..	4·54	—	—	—	—
Platinum ..	15·45	15·12	15·08	15·44	15·45

	Experiment. V.	VI.	VII.	VIII.	IX.
Carbon	—	—	54·66	54·68	—
Hydrogen ..	—	—	5·02	4·98	—
Platinum ..	15·02	15·60	—	—	15·49

	Experiment. X.	XI.	XII.	Average.
Carbon	54·38	—	54·85	54·64
Hydrogen ..	5·04	—	4·97	5·00
Platinum ..	—	15·12	—	15·26

The nitrate of ethyl-mauveine crystallises in beautiful crystals with a golden-green reflection.

I have already drawn attention to the existence of a second colouring matter in the mauve dye, differing from mauveine in its great solubility in alcohol. I have also mentioned that this is produced in the largest quantities when aniline of low boiling point is used. It is very difficult to free it from mauveine, as its solutions seem to act as solvents for the compounds of this colouring matter. I have made many experiments on this subject, and give an example of the processes used for its isolation.

A strong solution of the commercial mauve dye was first made by dissolving the dried paste in about three times its weight of boiling alcohol slightly acidulated, to this a small quantity of concentrated sulphuric acid was added, and the mixture allowed to stand two or three days. It was then filtered off from the sulphate of mauveine which had crystallised out. To the strong bronze-looking filtrate ether equal to about twice its bulk was gradually added, and after standing for a day or two the liquid was filtered off from deposited colouring matter, ether was again added, and after standing the solution filtered. A large excess of ether was then used, and the product set aside for some days. It was afterwards filtered, and the excess of the ether separated by distillation. The remaining purple solution was mixed with alcoholic potassic hydrate, added to boiling water, and heated until free from alcohol. The colouring matter which separated as a plastic mass was collected, washed, dried, and then dissolved in hot concentrated sulphuric acid to decompose or render soluble any impurities. The resulting green solution was diluted, and the precipitated colouring matter washed until the washings were but feebly acid and of a clear purple colour. It was then dissolved in boiling water, filtered, precipitated by the addition of sulphuric acid, and allowed to stand until cold; the precipitate was washed, redissolved, filtered, and again precipitated with sulphuric acid; when washed it was boiled with caustic potash, and, after removal of the alkali with water, dried. The black product was then dissolved in alcohol, with addition of a little potassic hydrate, and the solution filtered and evaporated to dryness. The resulting mass was ground with water, and was undoubtedly crystalline, as it gave the liquid a satiny aspect; it was finally well washed and dried. The following analyses were made with different specimens dried at 150° C.:—

I. ·3640 gram of substance gave
1·0569 „ of CO_2.

II. ·1900 „ of substance gave
·5520 „ of CO_2 and
·1000 „ of OH_2.

III. ·2608 gram of substance gave
·7516 „ of CO_2 and
·1270 „ of OH_2.

These numbers give percentages agreeing with the formula

$C_{24}H_{20}N_4$.

		Experiment.		
Theory.		I.	II.	III.
Carbon	79·12	79·18	79·21	78·59
Hydrogen	5·49	—	5·85	5·41

This base, which I propose to call *pseudo-mauveine*, differs from mauveine in being much more soluble in alcohol and in forming salts, which are also extremely soluble in that fluid. It is, however, like mauveine in being a very powerful base, and the combining with carbonic acid; it also dyes silk a shade of colour nearly identical with that produced with mauveine; and with concentrated sulphuric acid it forms a green solution, passing into blue and then purple on dilution. When heated it fuses, and yields a blue colouring matter.

Hydrochloride of Pseudo-mauveine.

This was prepared by dissolving the base in water very slightly acidulated with hydrochloric acid, filtering the purple solution, and precipitating by adding an excess of hydrochloric acid. The hydrochloride thus obtained was collected, washed, and dried. It was then dissolved in cold alcohol, filtered, and the solution evaporated to dryness. Thus obtained it has a greenish-golden reflection. It is more soluble in water than the hydrochloride of mauveine, and in alcohol it dissolves so freely that its solution may be obtained like a syrup with a bronze surface. Specimens of various preparations were examined, and gave the following numbers:—

I. ·3651 gram of substance gave
·9674 „ of CO_2 and
·1728 „ of OH_2.

II. ·3774 „ of substance gave
·9930 „ of CO_2 and
·1778 „ of OH_2.

III. ·3130 „ of substance gave
·8281 „ of CO_2 and
·1577 „ of OH_2.

IV. ·2221 „ of substance gave
·5868 „ of CO_2 and
·1143 „ of OH_2.

V. ·3280 gram of substance gave
·8648 „ of CO_2 and
·1718 „ of OH_2.

VI. ·2426 „ of substance gave
·6456 „ of CO_2 and
·1205 „ of OH_2.

		Experiment.		
Theory for $C_{24}H_{20}N_4.HCl$.		I.	II.	III.
Carbon	71·91	72·26	71·75	72·15
Hydrogen ..	5·24	5·25	5·25	5·59
	IV.	V.	VI.	Average.
Carbon	72·05	71·90	72·57	72·11
Hydrogen ..	5·71	5·82	5·51	5·52

The hydrochloride of pseudo-mauveine, when dissolved in alcohol and mixed with an alcoholic solution of platinic chloride, yields a platinum salt in the form of a black non-crystalline powder. On analysis it gave the following numbers:—

·2152 gram of substance gave
·0372 „ of platinum = 17·05 per cent.

The formula $(C_{24}H_{20}N_4)_2H_2PtCl_6$ requires 17·29 per cent.

From the analysis of pseudo-mauveine and its hydrochloride, it is evident that it cannot be regarded as a homologue of mauveine, as it contains two atoms of hydrogen too many for such a compound.

I have found that pure aniline obtained from benzene prepared from benzoic acid yields when oxidised a purple colouring matter, having apparently all the properties of pseudo-mauveine; as, therefore, this colouring matter contains twenty-four atoms of carbon, it appears probable that it is a derivative of aniline.* Of course one naturally hesitates in speaking too decidedly about the formula of such a substance as pseudo-mauveine, on account of not being able to prepare it in a definitely crystalline condition; still from the large number of analyses made of different preparations, it is difficult to see how it can be incorrect.

Some experiments have been made to show, if possible, the compounds from which ordinary mauveine is derived. From what has already been stated about its preparation, there could be no doubt that it was a derivative of aniline and toluidine, but the question unanswered was, is it para- or ortho-toluidine?

* It has already been mentioned that aniline containing but little toluidine yields a colouring matter of a bluer shade than that containing much toluidine. This blueness is due to the presence of some secondary products which are precipitated by ether in the purification of pseudo-mauveine.

Experiments were first made upon the oxidation of the sulphates of these two toluidines alone, and then in combination with aniline.

A mixture of solutions of the sulphate of paratoluidine and potassic bichromate, when allowed to stand, deposits a large quantity of a brown precipitate; this was collected, washed, and dried. On digesting it with benzene it gives to it a rich orange-red colour. This benzolic extract when distilled to a small bulk, deposits beautiful garnet-red crystals of a new azo-derivative, having the percentage composition of azotoluene, but possessing different properties. This substance is now under investigation. The residue left by the benzene, when digested with alcohol, yielded no colouring matter.

The sulphate of orthotoluidine treated in a similar manner gives a purple benzolic extract. This, when agitated with hydrochloric acid, gives up its colouring matter as a precipitate which dissolves in alcohol, with a dirty green colour, becoming indigo-blue on the addition of potassic hydrate.

The residue left after treatment with benzene gives a purple colour to alcohol; the amount of colouring matter, however, is small, and of a much redder shade than mauveine, even when purified.

A mixture of sulphates of aniline and paratoluidine in molecular proportions gives when oxidised a brownish-black precipitate. This gives to benzene a brown extract, but the residue treated with alcohol yields considerable quantities of mauveine, which can be obtained in a crystalline condition.

A mixture of sulphate of aniline and orthotoluidine in molecular proportions yields a very black precipitate, yielding to benzene a purple-brown colour. The residue gives up colouring matter to alcohol, but the amount is comparatively small, and the product of a very red shade of purple not at all like that of a mauveine salt.

Judging from these results it would appear that mauveine is derived from aniline and paratoluidine.

Oxidation of Mauveine.

When the commercial mauve dye is oxidised, it is converted, amongst other products, into a beautiful red colouring matter. It was first observed as a bye-product in the preparation of this colouring matter, but afterwards was manufactured in sufficient quantities to send into the market. It was, however, an expensive product. Originally it was called "aniline pink," but afterwards "safranine," a name which has since been applied to a similar colouring matter obtained from orthotoluidine.

To prepare this substance, the mauve dye was dissolved in water acidulated with acetic acid, the solution kept boiling, freshly precipi-

tated peroxide of lead was then thrown in little by little, until the oxidation had proceeded far enough; sodic hydrate was afterwards added in slight excess, and the product filtered. The red filtrate was next boiled for a short time with a little powdered zinc and carbonate of lime, again filtered, and then slightly acidified with hydrochloric acid, the precipitation of the colouring matter being rendered complete by the addition of sodic chloride. It was thus obtained as a red-brown precipitate, dissolving in water or alcohol with a splendid red colour.

I commenced the investigation of this substance several years since, and found that it consisted of the hydrochloride of an organic base, which I now propose to call *parasafranine*. To purify it for analysis it was dissolved in boiling water and rendered somewhat strongly alkaline with caustic alkali filtered from a small quantity of a purple colouring matter which had been precipitated and then thrown down by neutralising with hydrochloric acid and saturating the liquid with common salt. This process was repeated until all the purple-colouring matter had been separated. The product is the hydrochloride of parasafranine. If other salts are required I found it convenient in many cases to dissolve this hydrochloride in boiling water, render it alkaline with caustic alkali, and then acidify with the desired acid, and if necessary saturate the solution with a soluble salt of the acid used. The precipitated compound is then collected, washed, and crystallised. The oxalate prepared in this manner may be obtained in needles of a dark-green metallic aspect simply by adding oxalic acid and allowing the solution to stand. The nitrate also comes down readily on the addition of nitric acid.

In my earliest experiments I worked with the hydriodide of this colouring matter, because it was less soluble in alcohol than the hydrochloride, and thinking that perhaps it was a feeble base a little hydriodic acid was added each time it was crystallised. On analysis it was found that the more frequently it was recrystallised the lower the percentage of carbon came. At last a product was obtained which appeared to be definite, and gave numbers agreeing with the formula $C_{18}H_{18}N_4HI$. They are as follows:—

		Experiment.		
	Theory.	I.	II.	III.
Carbon	51·6	51·64	51·65	51·51
Hydrogen ..	4·5	4·57	4·51	4·39

After this, however, I obtained a specimen containing still less carbon, and this led me to discontinue working with this salt. I have not examined carefully into the cause of this change of composition, but it appears probable that it was due to the combiuation of the

hydriodide with free iodine from the oxidation of the hydriodic acid used.

I then examined other salts. A specimen of the hydrochloride of parasafranine was crystallised from alcohol, in which it was very soluble: it was obtained in a confused crystalline condition. It gave the following numbers on analysis:—

I. ·2605 gram of substance gave
·6492 „ of CO_2 and
·1305 „ of OH_2.

II. ·6265 „ of substance gave
·2586 „ of AgCl.

These give percentages agreeing with the formula $C_{20}H_{18}N_4.HCl$.

		Experiment.	
Theory.		I.	II.
Carbon	68·44	67·96	—
Hydrogen	5·42	5·56	—
Chlorine.....	10·41	—	10·21

Nitrate of Parasafranine.—This salt crystallises beautifully from alcohol in long needles with a dark-green metallic reflection, and when seen by strong transmitted light they appear of a dark garnet-red colour. It is rather difficultly soluble in cold water and only moderately so in boiling water. It is not very soluble in cold, but freely so in boiling alcohol. Specimens dried at 140—150° gave the following numbers:—

I. ·3005 gram of substance gave
·7016 „ of CO_2 and
·1400 „ of OH_2.

II. ·2284 „ of substance gave
·5320 „ of CO_2 and
·1104 „ of OH_2.

		Experiment.	
Theory for $C_{20}H_{18}N_4.HNO_3$.		I.	II.
Carbon	63·6	63·67	63·48
Hydrogen	5·04	5·15	5·37

The results of the analysis of these salts coincide with those lately published by Messrs. Dale and Schorlemmer in this Journal (p. 682).

The salts of parasafranine differ in solubility and crystallise better

than those of the safranine examined by Hofmann and Geyger. I find, however, that commercial safranine also contains a little parasafranine. The specimen I examined was made about four years since and obtained from Messrs. Guinon and Co. of Lyons. Some of this product was dissolved in a large quantity of boiling water and rendered strongly alkaline with caustic alkali; this caused most of the colouring matter to precipitate, but on filtration a strong red solution was obtained. The solution was acidified with nitric acid, and when cold the precipitate was collected, washed, and further purified by crystallisation from alcohol. On analysis it gave the following numbers:—

·2339 gram of substance gave
·5450 ,, of CO_2 and
·1132 ,, of OH_2.

These represent carbon 63·54 per cent. and hydrogen 5·37 per cent., and agree closely with those required by the formula $C_{20}H_{18}N_4.HNO_3$.

Silk dyed with this product was of the same shade as when dyed with the colouring matter from mauveine.

The safranine which had been precipitated with caustic alkali was dissolved in boiling water acidulated with acetic acid, filtered and precipitated with nitric acid; the nitrate thus obtained was crystallised from alcohol, and on analysis gave the following numbers:—

·2480 gram of substance gave
·5830 ,, of CO_2 and
·1240 ,, of OH_2.

These give percentages agreeing with the formula $C_{21}H_{20}N_4HNO_3$.

	Theory.	Experiment.
Carbon	64·45	64·11
Hydrogen	5·37	5·55

Safranine salts differ from those of parasafranine in the colour they dye silk, yielding shades which are somewhat more scarlet.

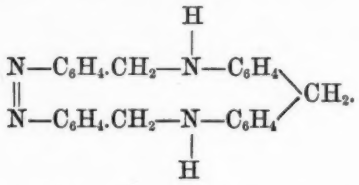
Pseudo-mauveine, when oxidised, yields a colouring matter similar to parasafranine. This is probably present in the product obtained by oxidising the commercial mauve dye, but lost in the after processes of purification.

Up to the present very little is known of the constitution of mauveine, but there can be no doubt it is derived from aniline and paratoluidine.

Hofmann has shown that safranine is derived from 3 molecules of orthotoluidine; now as parasafranine contains one atom less of carbon than this compound, and is derived from mauveine, it is more than pro-

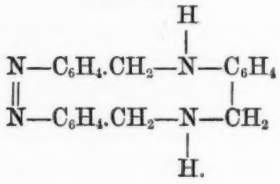
bable that it is formed from 2 molecules of paratoluidine and 1 molecule of aniline; and as mauveine contains 7 atoms more carbon, it would be a derivative of 3 molecules of paratoluidine and 1 molecule of aniline; this would also be gathered from its containing 27 atoms of carbon.

Now, as aniline and also paratoluidine yield azo-derivatives when oxidised, it is very probable that mauveine may belong to that class of compounds, and, if so, might perhaps be represented thus :—

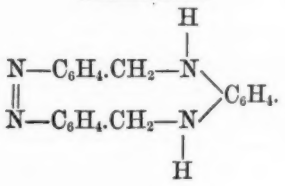


Safranine and parasafranine might also be represented in a somewhat similar manner :—

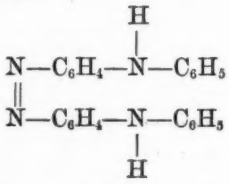
Safranine.



Parasafranine.



And pseudo-mauveine as—



I bring these forward merely as suggestions; experiment alone can settle the true constitution of these bodies. I am at present making some experiments upon the acetylic replacement-derivatives of mauveine and safranine, which I hope may throw a little additional light upon the matter.

LXXV.—*On the Action of Sulphuric Acid on the Hydrocarbons of the Formula $C_{10}H_{16}$.*

By Henry E. Armstrong, Ph.D., F.R.S., and William A. Tilden, D.Sc. (London).

I. *The Nature of Terebene, Terpilene and Colophene.*

The action of sulphuric acid on (oil of) turpentine appears to have been first studied by Deville (*Ann. Chim. Phys.*, 1840, **75**, 37). According to this chemist, the turpentine is partly converted into *terebene*, an optically inactive hydrocarbon of the same composition and boiling point (about 160°) as the original oil; and is partly converted into *colophene*, a polymeric hydrocarbon probably of the formula $C_{20}H_{32}$.

The reaction did not attract further notice for a long time, and excepting a casual reference by Berthelot (*ibid.*, 1853 [3], **38**, 42) to Deville's experiments, which he apparently confirms, no further mention of it occurs prior to 1873, when it was again investigated by Riban (*Compt. rend.*, **76**, 1547) in the course of his important researches on the terpene of French turpentine and the isomeric hydrocarbons derived from it (in extenso, *Ann. Chim. Phys.*, 1875 [5], **6**, 5, 215, 353, 473); a short account of experiments on the same subject by Orlowski was published a few months after the appearance of Riban's paper (*Deut. Chem. Ges. Ber.*, **6**, 1257).

Riban confirmed Deville's conclusion that terebene was an isomeride of the terpene from which it was prepared, but showed that the properties ascribed to it by Deville were not those of a pure substance, but of a mixture containing much cymene, whence the formula $(C_{10}H_{16})_2HCl$ assigned to its liquid hydrochloride by the latter chemist. Orlowski arrived at a similar conclusion: according to this chemist, the product contains more cymene than terebene.

Riban's "terebene" remained liquid even at −27°, and had practically the same density, boiling point (156°), and refractive index as the terpene from which it was prepared, the only physical difference between them being in their behaviour with polarised light; but whereas terpene monohydrochloride was found to melt at 131—132°, and to be decomposed only to a very slight extent on prolonged heating with water at 100°, "terebene" monohydrochloride was found to melt at 125°, and to be very rapidly and completely decomposed by water at 100°, manifesting in this respect the very closest resemblance to the monohydrochloride obtained from inactive camphene, which, however, melts at 145°, the curves representing the decomposition of

the two substances by water as a function of the time of heating being almost coincident. It is noteworthy also that, according to Riban, "terebene hydrochloride" is decomposed even by prolonged washing with cold water, yielding *solid camphene* and hydrochloric acid, whereas when decomposed by water at 100° it yields liquid "terebene."

Theoretical considerations and the desire to investigate "terebene" in other directions led us independently to re-examine the action of sulphuric acid on the hydrocarbons of the formula $C_{10}H_{16}$, and finding that we were both thus engaged, we judged it desirable to associate in carrying on the investigation.

We have employed chiefly American turpentine, but have confirmed all the results obtained with this terpene with French turpentine, as this latter was employed by Riban, and doubtless also by Deville. We have also made a number of experiments with the hydrocarbons derived from various essential oils, but in the present communication we shall confine ourselves chiefly to the results afforded by the terpenes of American and French oil, describing them under the following heads:—

I. Action of sulphuric acid of various degrees of concentration on terpenes.

II. Examination of crude "terebene," the volatile optically inactive product of the action of concentrated sulphuric acid on terpenes.

III. Examination of the volatile optically inactive product of the action of dilute sulphuric acid on terpenes.

IV. Behaviour of "colophene" on distillation; examination of the colophene distillate.

V. Discussion of the results.

VI. Oxidation of camphene.

VII. Summary.

We should here state that we term only those hydrocarbons of the formula $C_{10}H_{16}$, *terpenes*, which boil at about 156°, and of which American and French turpentine oils may be taken as the type.

§ I. *Action of Sulphuric Acid of various Degrees of Concentration on Terpenes.*

The method originally employed by Deville in preparing "terebene" consisted in carefully mixing the turpentine with concentrated sulphuric acid in a retort, and submitting the mixture to distillation after the violent spontaneous action which takes place had subsided; the distillate was then distilled, and the portion passing over below about 210—220° was treated in a similar manner, and these opera-

tions were several times repeated, if necessary, until finally an optically inactive product was secured.

In a postscript to his memoir (*op. cit.*, p. 79) Deville, however, recommends a modified method. The turpentine is to be gradually mixed with $\frac{1}{20}$th of its weight of acid, and the mixture thoroughly agitated, the reaction being moderated by cooling the vessel in which the operation is conducted; after 24 hours, the product is to be decanted from the acid and distilled, and the distillate is to be again similarly treated, &c.

This latter method was adopted by Riban, who continued the distillation of the crude product until the temperature rose to about 250°. From *five* to *eight* treatments with acid, &c., are necessary, according to this chemist, to entirely deprive the terpene of its optical activity.

In all our experiments we have adopted a somewhat less destructive method, and instead of distilling the crude product of the action of the acid *per se*, we have submitted it to steam-distillation; *i.e.*, it was placed in a flask or other convenient vessel, together with sufficient soda to neutralise the adhering acid, and a rapid current of steam passed through the liquid, the flask being gently heated on the sand-bath in order to prevent the condensation of the steam. In this manner, a much more perfect separation of the unaltered terpene and of the "terebene" from the "colophene" is effected, and secondary decompositions are entirely avoided.

It will be convenient, in describing the results of experiments with acid of various degrees of concentration, to employ the terms 1 : 1, 2 : 1, 4 : 1 acid, &c., as indicating mixtures of acid and water in the proportions of 1 : 1, 2 : 1, 4 : 1, by volume.

It appeared probable, since "terebene" is itself acted upon by sulphuric acid, that a better yield of "terebene" might be secured by using a somewhat diluted acid, and by avoiding as much as possible a rise of temperature during the reaction. A large number of experiments were therefore made under very different conditions in order to ascertain the influence both of concentration of the acid, and of temperature, on the course of the change. A few of these may be here described in detail.

Five quantities of 25 c.c. each of concentrated sulphuric acid were diluted with 25, 20, 15, 10 and 5 c.c. of water respectively, and each of these was added to 500 c.c. of French turpentine, rotating about −59° per 200 mm.* The mixture was placed in a stoppered bottle, and vigorously agitated at frequent intervals during an hour; the

* In all cases the rotatory power of a 200 mm. column was observed. One of us used a Wild, the other a Jellet-Cornu or a Laurent polarimeter, the source of light being a "sodium-flame."

product was then steam-distilled, and the rotatory power of the distillate determined.

(*Experiment* 1.) 5 : 5 *Acid.*—Temperature rose only about 2°. On steam-distilling, 468 c.c. were recovered, having practically the same rotatory power as the original terpene. 450 c.c. of this product were added to 200 c.c. of 1 : 1 acid, and the mixture agitated at frequent intervals during two working days; 350 c.c. were recovered, having a rotatory power of 55° 10′. This latter product again treated in a similar manner gave 275 c.c., rotating 47°. In the last case, after agitating the mixture when first made for several minutes, the temperature rose only 3—4°.

(*Experiment* 2.) 5 : 4 *Acid.*—Temperature rose from 15° to about 60°: recovered 375 c.c., rotating 46° 4′.

(*Experiment* 3.) 5 : 3 *Acid.*—Temperature rose but little higher than in the previous experiment: recovered 330 c.c., rotating 45° 40′. It was necessary in this experiment to transfer the mixture to another bottle, which produced considerable cooling. Probably a slightly different result would have been obtained had this not been the case.

(*Experiment* 4.) 5 : 2 *Acid.*—Temperature rose to 115° almost immediately on shaking; allowed to cool to about 70° before continuing agitation. Recovered 265 c.c., rotating 24° 20′.

(*Experiment* 5.) 5 : 1 *Acid.*—Added 10 c.c., and shook for a couple of minutes; temperature rose nearly to the boiling point of the terpene. The remaining 20 c.c. of acid were afterwards added. Recovered 130 c.c., rotating 3° 50′.

These experiments show clearly that the amount of colophene produced increases with the concentration of the acid. The rotatory power is almost destroyed by the 5 : 1 acid, but it is noteworthy that by the action of less concentrated acids it is only diminished by about one-fifth to two-fifths; it would seem therefore that the chief tendency of somewhat dilute sulphuric acid is to polymerise the terpene.

Precisely similar results were obtained in a number of experiments with American turpentine, having a rotatory power of about 30° per 200 mm.

Following the indications afforded by these results, the action of the concentrated acid was now investigated. In one experiment (*Experiment* 6), using 500 c.c. American oil and 20 c.c. acid, 265 c.c. were recovered, having a rotatory power of about 4°. In a second experiment with 25 c.c. acid (*Experiment* 7), 150 c.c. of an entirely inactive product were obtained. In a similar experiment with 500 c.c. French turpentine and 25 c.c. acid (*Experiment* 8), 140 c.c. were recovered, rotating about 1°. In these experiments, the acid was added by 5 c.c. at a time, and the mixture then well agitated until the temperature

sank to a point at which it was judged advisable to add a further quantity of acid; thus in the case of the first, the temperature rose from 21 to 118° on agitating with the first 5 c.c. of acid; the second 5 c.c. were added at 80°, and caused a rise of temperature to 122°; on adding the third 5 c.c. at 85° and agitating, the temperature rose only to 113°; the fourth 5 c.c. caused a rise in temperature from 87 to 103°.

In order to ascertain the influence of temperature, two experiments were made—one with American (*Experiment* 9), the other with French oil (*Experiment* 10)—in which the terpene was placed in a copper flask surrounded with ice, and treated with 25 c.c. concentrated acid added by 5 c.c. at a time. The flask was frequently agitated, but each time for a very brief period, so as to avoid a rise in temperature. After about six hours the product was steam distilled. The American oil gave 302 c.c., rotating 22° 20′; the French oil 247 c.c., rotating −46° 50′. Again, two quantities of 500 c.c. of American turpentine rotating 33° 10′ had each 10 c.c. of concentrated acid added to them. One portion (*Experiment* 11) was then vigorously agitated, which caused the reaction to take place with such rapidity that spontaneous ebullition of the turpentine set in, and continued for some little time; the steam distillate from this portion had a rotatory power of 7° 48′. The other portion (*Experiment* 12) was more carefully agitated, so that the temperature never rose to the boiling point; the steam-distillate obtained from it had a rotatory power of 11° 3′.

It is evident, therefore, that in order to obtain the maximum amount of inactive product it is necessary to employ concentrated acid, and to allow the action to proceed at an elevated temperature. Our experience leads us to believe that the following is probably the best method of preparing crude "terebene":—Several capacious flasks—four is a convenient number—are each charged with a litre of the terpene,* and 10 c.c. of acid are added to the first flask, and its contents thoroughly agitated; the others are then treated in succession in a similar manner, and from time to time each is well shaken. When the temperature sinks to about 80—90°, a second 10 c.c. of acid are added, and the mixture again agitated from time to time. In like manner a third, fourth, and fifth portion of 10 c.c. of acid is added to each flask.† After standing several hours, the product is separated, as

* Steam-distilled turpentine should be used.

† The rise in temperature is the only outward manifestation of a reaction. Should the action become too violent and the turpentine enter into ebullition, as sometimes happens when the acid is added too rapidly, it is desirable to allow it to abate spontaneously, as any attempt to cool the flasks is almost sure to result in their fracture; in fact, the yield is better the less the development of heat is checked and the more rapidly the conversion is effected.

far as possible, from the acid, and steam-distilled as before described.* Frequently the distillate thus obtained has a slight rotatory power, but this should never exceed from 2—3° per 200 mm.; in order to render it inactive, it is again treated with acid in the proportion of 10—20 c.c. per litre, the mixture being violently shaken for some time in a stoppered bottle. If after this the product still manifests optical activity it must be again treated with acid, but it is very desirable to effect the conversion as completely as possible in the first instance, as each fresh treatment with acid involves the loss of a considerable amount of the "terebene." Provided sufficient acid is used, the success of the operation depends on the thoroughness with which the acid and terpene are brought into contact by agitation, and on the temperature being kept high; even in the most successful experiments, however, the amount of inactive product seldom exceeds 20—25 per cent. of the terpene employed.

The following account of experiments will give some idea of the difficulty of obtaining an inactive product, and will serve to exhibit also the uniformity of the results furnished by successive operations under similar conditions. Of 23 litres American turpentine treated with 50 c.c. 2 : 1 acid per litre (the treatment was effected before we had finally ascertained that it was desirable to employ the concentrated acid):

(*Experiment* 13.)

2	litres	gave	1,505 c.c.
4	„	„	3,140 „
4	„	„	3,010 „
4	„	„	3,280 „
4	„	„	3,160 „
5	„	„	3,930 „

or an average yield of 783 c.c. per litre. The rotatory power of these distillates varied between 21° and 23°. This product was treated with concentrated acid.

(*Experiment* 14.)

a.	4	litres	with 50	c.c. acid	per litre	gave 2,160 c.c.
b.	4	„	55	„	„	2,090 „
c.	4	„	55	„	„	2,090 „
d.	5·5	„	60	„	„	2,450 „

a, *b*, and *c* had a rotatory power varying but little from 3°; the rotatory power of *d* was about 1°.

1 litre of *d* well shaken for a considerable time in a Winchester

* We have found an iron retort constructed from a two gallon Papin's digester of the greatest service for this purpose.

quart with 15 c.c. 4 : 1 acid gave 950 c.c. of almost undiminished rotatory power. On treatment with 10 c.c. concentrated acid, this gave 730 c.c. of inactive product.

1 litre of *d* was heated to about 65°, and then agitated with 10 c.c. concentrated acid; the temperature rose only about 10°, and 770 c.c. were recovered rotating about 1°. It does not appear therefore that any advantage is to be derived from heating. The 770 c.c. gave 520 c.c. of inactive product on agitation with 10 c.c. of concentrated acid.

a, *b*, and *c*, together with a small quantity of similar product from another operation, gave the following results:—Two portions, each 1,150 c.c., with 15 c.c. acid per portion, gave 2,026 c.c., rotating about 1° 30′; and three equal portions, together 3,470 c.c., each with 15 c.c. acid, gave 3,000 c.c. of nearly the same rotatory power. Lastly, 5,200 c.c., the activity of which was about 1° 30′, treated in three equal portions with 20 c.c. per portion, gave 4,460 c.c. of inactive product.

(*Experiment* 15.)—4,800 c.c. French turpentine, treated with 50 c.c. concentrated acid per litre, gave 1,645 c.c., rotating 5° 20′; this was rendered inactive by two successive treatments with 10 c.c. of acid, but at a loss of over one-third.*

An inactive product may, however, be obtained in a single properly conducted operation. Thus, on one occasion, 9 litres of American turpentine were treated in two portions of 2 litres, and two portions of 2·5 litres, with concentrated acid, added by 25 c.c. at a time, till 100 c.c. had been used to each of the former, and 125 c.c. to each of the latter; the steam distillate was inactive, the average yield being 257 c.c. per litre of turpentine.

A part of the acid employed dissolves in the terpene, but a part appears to remain merely in contact with it, and rapidly subsides to the bottom of the vessel when agitation is interrupted. It is therefore remarkable that immediate further action at once takes place if a fresh quantity of acid be added when the reaction produced by that previously added has passed the maximum, or even when it is practically at an end, and the liquid has cooled down to the atmospheric temperature; it would almost appear that the acid becomes "soiled," and incapable of further acting except with extreme slowness. If the acid which deposits is mixed with water, a brown or black viscid matter separates, but the quantity is so small that it can-

* We have several times noticed on treating French and American turpentine with 2 : 1 acid under precisely similar conditions, that the action sets in less rapidly with the French than with the American turpentine, although when the change has once commenced it would seem to proceed with equal readiness in both cases, and to be attended with the development of about the same amount of heat.

not be supposed that the inactivity of the acid is due to the formation of a sulphate which is decomposed by water; and if the acid solution is neutralised with barium carbonate, filtered, and evaporated to dryness, an amount of solid residue is obtained, which bears no proportion to the amount of acid taken. The result is also the same if the acid which deposits is separated when it has produced the maximum effect before a further quantity is added. That this is the case is shown by the two following experiments with American turpentine rotating 33° 10′, in each of which the undissolved acid was separated before the addition of a fresh portion. The experiments differ only in that in one case a further quantity of acid was added soon after the maximum effect had been produced, but in the other only after the liquid had cooled down almost to the atmospheric temperature. 1 litre of turpentine was used in each instance:

(*Experiment* 16.)

	Initial temperature.	Temperature of maximum effect.	Amount of acid undissolved.
1st 10 c.c. of acid....	17°	72°	4 c.c.
2nd „ „	20	53	3 „
3rd „ „	20	50	4 „
4th „ „	25	54	4 „
5th „ „	25	54	10 „
			25 „

(*Experiment* 17.)

1st 10 c.c. of acid....	20°	78°	5 c.c.
2nd „ „	63	130	4 „
3rd „ „	70	105	4 „
4th „ „	70	90	5 „
5th „ „	75	95	11 „
			29 „

The steam distillate from Experiment 16 measured 465 c.c., and had a rotatory power of 9° 20′; that from Experiment 17 measured 282 c.c. and was inactive.

The "dissolved" acid appears only to exert an action initially. Thus 500 c.c. turpentine were treated with 10 c.c. acid, and when the mixture had almost cooled down to the atmospheric temperature, about 100 c.c. were withdrawn; the remainder having been carefully separated from the undissolved acid—about 5 c.c., was heated in the water-bath for about three and a half hours. The steam-distillate from the 100 c.c. withdrawn previous to heating, and that from the product after heating, had, however, the same rotatory power.

As before remarked, even if the turpentine be submitted to the prolonged action of the undissolved acid, this latter has but little action beyond that which it exerts when first brought into contact with the terpene. Thus the rotatory power of 500 c.c. of turpentine was reduced by treatment with 10 c.c. acid from 33° 10′ to 11° 3′; but on heating about 400 c.c. of the oil together with the undissolved acid—apparently about half that employed—for three and a half hours in the water-bath, the rotatory power fell only to 9° 19′.

The amount of acid dissolved varies in different experiments; on one occasion, on adding 30 c.c. acid to 3 litres of turpentine, it was observed that the whole dissolved, but this seldom occurs. The above-quoted experiments, in which the deposited acid was removed before acid was again added, show that the acid dissolves only as the reaction progresses; and it would seem, therefore, that a substance is produced in the course of the change which is capable of dissolving or fixing it. There can be little doubt that this is actually the case, for we have frequently in the course of our experiments had occasion to notice the formation in small quantity of what appear to be acid sulphates analogous to ethyl-hydrogen sulphate. For example, 217 c.c. of a fraction of the product of the action of sulphuric acid on turpentine boiling at about 156°, were treated with 60 c.c. 2 : 1 acid, added gradually. On mixing the product with water, an oil separated which was shaken with a solution of soda, but, on standing, only 135 c.c. of oil rose to the surface, leaving the soda-solution clear; the alkaline liquid drawn off and acidified gave about 200 c.c. of a liquid which floated to the surface. This liquid was completely soluble in about four times its bulk of water, but was precipitated as an oil by the addition of very little more; it was perfectly clear till heated to about 70°, when it became turbid, and separated into two layers, which would not reunite on cooling; it was also completely soluble in potassium carbonate solution with effervescence, and its saturating power for alkalis was increased, although not doubled, by heating to complete decomposition; it formed a soluble, gummy barium salt, which, however, very readily decomposed. On repeating the experiment, we never again succeeded in preparing so large a quantity of this substance, and attempts to extract such a body from the crude product of the action of sulphuric acid on turpentine were almost uniformly unsuccessful.

A mixture of equal volumes of concentrated acid and water, as we have already pointed out (p. 736), acts very slowly at ordinary temperatures, and tends chiefly to polymerise the terpene. As a number of observations, made in the course of our experiments, appeared to indicate that the inactive product of the action of dilute acid was different from that resulting from the action of concentrated acid, we endea-

voured to render the terpene inactive by means of 1 : 1 acid, and finally succeeded in doing so by heating it and the acid together in a stoppered bottle at about 80°, and frequently agitating so as to bring them into contact. But even under these conditions the change takes place very sluggishly, and it is especially difficult to destroy the last traces of activity; the conversion is facilitated if, once or twice during the operation, the oil is separated from the acid and steam-distilled so as to remove the colophene. Finally, after several days' heating, an amount of inactive product is obtained on steam distilling the crude product equal to from one-third to one-half the volume of terpene originally taken. Since our experiments were made, a short account of similar observations by Flawitzky has been published (*Deut. Chem. Ges. Ber.*, **12**, 1022).

It deserves to be mentioned that on more than one occasion we have observed a distinct increase in the rotatory power of American turpentine on heating it in the water-bath for a short time with 1 : 1 or 1 : 2 acid; a similar change has been noticed in the case of Russian, but not with French turpentine. This would appear to indicate that American turpentine contains a substance which either has a less dextrorotatory power, or is lævorotatory, and which is more readily polymerised than its chief constituent.

§ II. *Examination of Crude "Terebene," the Volatile Optically Inactive Product of the Action of Concentrated Sulphuric Acid on Terpenes.*

According to Riban (*op. cit.*, p. 234), the product of the action of sulphuric acid on French turpentine is resolved by fractional distillation (1) "en térébène bouillant à 156°; (2) en cymène vers 175°; (3) dans certains cas, en une petite quantité de matière camphrée de 190—205°; (4) en colophène et produits supérieurs bouillant à partir de 300°." The "terebene" and cymene are contained in the portion of the crude product boiling between 155° and 200°, and are separated by long-continued fractional distillation, finally from sodium; the ultimate result being to resolve this portion of the product (1) "en térébène bouillant vers 156°, en cymène vers 175°, et en une petite quantité de liquide intermédiaire entre ces deux températures, mélange inséparable des deux carbures. Le rendement en térébène sensiblement pur est de 10 pour 100 au plus du poids du térébenthène primitif; le cymène représente 6 à 8 pour 100 du carbure initial. Le reste est constitué par des polymères et autres corps formés sous l'influence de l'acide sulfurique. Le rapport entre la quantité de térébène et de cymène obtenus varie d'ailleurs avec les doses d'acide sulfurique employées successivement. Un excès d'acide tende à exagérer la formation des polymères et du cymène, de telle sorte que, dans certaines

opérations, la quantité de ce dernier peut égaler et même dépasser celle du térébène obtenu."

The properties of "terebene" are said by Riban to be as follows:—"Le térébène est une liquide incolore, mobile, d'une odeur faible, difficile à définir, mais qui ne rappelle en aucune façon celle du thym. Il ne se congèle pas à une température de −27°, longtemps soutenue."

According to Orlowski (*loc. cit.*), the portion boiling at 160—210° of the distillate from the product obtained by treating turpentine with sulphuric acid until inactive, yields on repeated distillation two liquids of constant boiling point: "terebene" boiling at 155—157°, and cymene boiling at 174—176°.

The following account of our results applies to the inactive distillate obtained on passing steam through the crude product of the action of sulphuric acid, which it will be convenient to speak of as crude "terebene;" for reasons to be described later on, we purposely avoided distilling the polymerised product until entirely freed from substances volatile in a current of steam. In all other respects, our method of operating has been identical with that adopted by Riban.

Operating on a quantity of 6,700 c.c., prepared from American turpentine, it was found that after long-continued fractional distillation the greater part boiled at about 155—160° (*b*), and at 175—180° (*c*), although the intermediate fractions were considerable in amount; a few c.c. only were collected below 154° (*a*); and the amount passing over above 180° was comparatively small (*d*).

a. The substance or substances of low boiling point in the fraction collected below 154° are probably either derived from the turpentine, as we have frequently noticed on distilling turpentine that a very small quantity of some substance of much lower boiling point first passes over; or, which is more probable, they result from the decomposition of the oxidation-product which is formed during the distillation. This portion of the distillate has a peculiar sweet smell.

b. The portions boiling at temperatures near to 160° were submitted to a most rigorous fractional distillation from sodium,* partly with the aid of the Le Bel and Henninger apparatus, partly with the simpler form of fractioning column described by one of us, and ultimately we had the satisfaction of seeing the distillate passing over at about 158—159° completely solidify in the condenser, and we found it easy to cause some of the less highly fractioned portions to solidify more or less completely by cooling with ice or with ice and salt. The substance thus obtained is undoubtedly identical with the inactive *camphene* which Riban prepared by heating his "terebene" hydrochloride

* A quantity of brown matter separates out when the various fractions, even the lowest, of crude terebene are distilled from sodium.

with sodium stearate at 180°. After being well pressed between filter-papers, it fused at 40°; but the melting point was raised to 47° by a single crystallisation from alcohol, from which it separates in crystals like those of ammonium chloride.

According to Riban, "terebene" hydrochloride melts constantly at 125° in an atmosphere of hydrochloric acid gas, whereas the hydrochloride of inactive camphene melts under similar conditions at 145°. The hydrochloride prepared from our product in the manner described below, and dried by prolonged exposure over calcium chloride, was found to melt at about 118°; but after purification by careful sublimation in a current of perfectly dry hydrochloric acid gas, it fused at about 145°, *i.e.*, at the same temperature as Riban's camphene hydrochloride.

The behaviour of American turpentine with sulphuric acid has not, so far as we are aware, been previously examined, and the difference between our result and Riban's might therefore be ascribed to our having used American instead of French turpentine. To meet this objection, a quantity of the latter was rendered inactive by treatment with concentrated acid, and from about a litre of inactive product we succeeded in isolating with comparatively little trouble a fraction boiling at 158—160°, which deposited crystals of camphene when cooled to about −15°; the fraction at 156—158° remained liquid when similarly treated.*

Riban has stated that when "terebene" hydrochloride is decomposed by cold water or by heating with sodium stearate at 180°, it yields solid camphene; but that if it is decomposed by heating with water or an alcoholic solution of potassium hydroxide at 100°, "terebene" is regenerated: the "terebene" produced in this last-mentioned manner being liquid at − 27°. We have repeated the experiment and find, as was to be expected, that camphene ("terebene") hydrochloride regenerates camphene when thus treated. 200 c.c. of fractions collected at 156—158°, which remained liquid at the ordinary atmospheric temperature, were mixed with an equal volume of anhydrous methylated spirit, and the mixture saturated with hydrochloric acid gas; after some time, it became nearly solid from the separation of the hydrochloride. The crystals were thoroughly drained on a vacuum filter, once washed with spirit, and well pressed between folds of bibulous paper. 160 grams of the hydrochloride thus prepared were

* The boiling point of camphene, according to Riban, is 156—157° (corr.). We have observed that the camphene crystallises most readily from the fractions of crude "terebene" collected near to 160° (the stem of the thermometer being entirely immersed in the vapour); whether therefore the boiling point of camphene is somewhat higher than has been stated, or whether this is because the foreign substance of lower boiling point associated with the camphene exercises a greater influence than that of higher boiling point in hindering crystallisation remains to be decided.

heated with 150 grams of potassium hydroxide and 250 c.c. anhydrous methylated spirit in an iron digester for about 20 hours at 110°; on steam-distilling the product, 140 c.c. of hydrocarbon were obtained. This began to boil at about 155°, but very little came over below 157°; at this point the distillate began to solidify in the condenser, and ultimately fully four-fifths of the entire product were obtained as a solid mass of camphene. It is difficult to understand how Riban can have failed in causing the distillate to solidify at −27°.

There can be no doubt therefore that "terebene" does not exist as a distinct substance, and that Riban's "terebene" was merely slightly impure inactive camphene.

c. A very large proportion of the crude terebene obtained either from American or French turpentine—*fully two-thirds*—boils above 170°, the greater part passing over between about 175° and 180°. This, however, does not consist, as Riban and Orlowski have stated, entirely of cymene, but is principally *terpilene*, the liquid optically inactive isomeride of the terpenes which may be obtained by the decomposition of the dihydrochlorides of the $C_{10}H_{16}$ hydrocarbons by sodium (Berthelot) or by heat, and by the action of dilute sulphuric acid on so-called terpin, $C_{10}H_{18}(OH)_2 + OH_2$ (comp. Tilden, this Journal, 1878, **33**, 250). This portion of the distillate also contains a relatively small quantity of a paraffin-like hydrocarbon of the formula $C_{10}H_{20}$*, which boils at about 170°. About 80 per cent. of the crude "terebene" is polymerised on treatment with 4 : 1 acid, and the amount of cymene and of the hydrocarbon $C_{10}H_{20}$ in it therefore certainly does not exceed 20 per cent.; of this about three-fourths is soluble in concentrated sulphuric acid, so that the amount of the hydrocarbon $C_{10}H_{20}$ in crude "terebene" may be estimated at about 5 per cent.

The presence of terpilene in the fractions collected at 175—180° is indicated by their possessing its characteristic odour and by their behaviour with 4 : 1 sulphuric acid. Acid of this strength is entirely without action on cymene but polymerises terpilene. If the fractions in question are agitated with about an equal bulk of acid, considerable heat is developed, and on afterwards steam-distilling the product, the greater part is found to be converted into a non-volatile substance (colophene); if the distillate be again similarly treated, it is usually unaffected, and in this case consists only of cymene and the hydrocarbon $C_{10}H_{20}$.

According to Berthelot, terpilene prepared by the action of sodium on turpentine dihydrochloride yields a crystalline dihydrochloride on treatment with hydrochloric acid. We completely failed in obtaining a dihydrochloride by the ordinary method from the terpilene

* This hydrocarbon is being studied by one of us.

University of Michigan

separated from crude "terebene" and also from that obtained from terpin; finding, however, that the terpilene from crude terebene gave Riban's reaction for the dihydrochlorides,* and having ascertained that the dihydrochloride from orange oil could be steam-distilled in presence of hydrochloric acid for the most part unchanged, we endeavoured to separate the terpilene dihydrochloride by fractional distillation in a current of steam. The crude terpilene, *i.e.*, the mixture of the hydrocarbon with cymene and the $C_{10}H_{20}$ hydrocarbon, was mixed with about an equal volume of ether, the solution saturated with hydrochloric acid gas, and then steam-distilled. The oil passing over with the steam during the earlier part of the distillation was lighter than water, but that collected during the later part just sank in water:† on cooling this latter to about $-12°$ and then introducing a minute fragment of the crystalline dihydrochloride from orange oil, the whole solidified to a mass of glistening scales. These crystals exactly resembled those of the dihydrochloride prepared from orange oil, and had the same melting point (52°).

The terpilene which gave this result had been separated from the crude terebene obtained from American turpentine, in preparing which 2 : 1 acid had been partially employed (see p. 738); but the fraction collected at 175—180° of crude "terebene," prepared from French turpentine entirely by the action of concentrated sulphuric acid, furnished a precisely similar product of the composition $C_{10}H_{18}Cl_2$ when treated in the same manner.

d. After long-continued fractional distillation of crude "terebene" a relatively very small quantity is found to boil above about 180°. A considerable portion of this high-boiling product does not volatilise in a current of steam. Judging from its properties and bearing in mind that originally the whole of the crude "terebene" had been distilled in steam, we believe that the distillate above 180° is not a product of the action of sulphuric acid, but consists at least mainly, if not entirely, of substances formed by oxidation during the long-continued fractional distillation to which the crude "terebene" is subjected. By exposure to air, the hydrocarbons of the formula $C_{10}H_{16}$ are all gradually converted into a viscid oxidised body which does not volatilise in steam, terpilene

* This reaction is extremely sensitive and consists in triturating in a porcelain dish a particle of the dihydrochloride with a drop of concentrated solution of ferric chloride, and very carefully warming the mixture; a rose colour is produced, which soon changes to a reddish-violet, and finally to blue. It is not necessary, however, to prepare the dihydrochloride; a drop of the hydrocarbon capable of yielding it may be mixed with a drop of hydrochloric acid and with the ferric chloride.

† By saturating the portion which floats on water with hydrochloric acid gas, and steam-distilling it together with ordinary concentrated hydrochloric acid solution, a further quantity of dihydrochloride may be obtained.

undergoing oxidation in this manner with especial readiness; this body is decomposed by distillation, yielding a considerable proportion of products volatile in a current of steam, but boiling chiefly towards about 200°. In odour, appearance, and general behaviour, the high-boiling portions of the crude "terebene" distillate are not to be distinguished from those of the distillate from the oxidation-product in question; moreover, when treated with 4 : 1 sulphuric acid, they are for the most part converted into a non-volatile resinous product, but on pouring the acid into water, a small quantity of oil separates, which, if purified by steam-distillation, has a strong peppermint-like odour, and is also characterised by yielding a dark purple colour when brought into contact with concentrated nitric acid.

Riban states that on one occasion the fraction boiling at 190—210° deposited a small quantity of a substance possessing all the exterior properties of camphor, and fusing at 169°. We have several times noticed, on separating the crude "terebene" from the colophene by steam-distillation, that a small quantity of such a substance separates from the last portions of the distillate. After being dissolved in 4 : 1 sulphuric acid, precipitated by water and steam distilled, it was found to melt at 172°. There is no doubt that this substance is camphor; we have not been able to detect it, however, in the fraction *d*.

§ III. *Examination of the Volatile Inactive Product of the Action of Dilute Sulphuric Acid on the Terpenes.*

The product of the action of 1 : 1 acid on American or French turpentine begins to boil at about 170°, and the greater part passes over between 175° and 185°. The amount collected below 170°, after prolonged fractional distillation from sodium, is very small, and we have failed in obtaining any evidence of the presence of camphene in this portion of the distillate.

The quantity collected between 170° and 176° is also inconsiderable; the main portion of the product boils at 176—180°. This latter consists principally of terpilene, about 80 per cent. being converted into colophene by the action of 4 : 1 acid; the portion unaffected by acid of this strength is cymene mixed with a few per cent. of the hydrocarbon $C_{10}H_{20}$. Crystalline terpilene dihydrochloride may be obtained from this fraction by operating in the manner previously described.

Although the amount passing over at the first distillation above 180° is much diminished by prolonged fractioning from sodium, a by no means inconsiderable quantity is finally obtained boiling between this temperature and 190°. In this respect, the product of the action of 1 : 1 acid closely resembles the crude terpilene formed by treating terpin with dilute sulphuric acid (comp. Tilden, this Journal, *loc. cit.*).

Apparently an oxygenated substance is formed which is not attacked by sodium.*

We have not specially examined the volatile inactive product of the action of acid intermediate in strength between the 1 : 1 and the concentrated acid, but we have ascertained that a small quantity of camphene is formed on treating turpentine with 2 : 1 acid. Probably the amount of camphene produced increases with the concentration of the acid.

§ IV. *Behaviour of "Colophene" on Distillation; Examination of the Colophene Distillate.*

We apply the term "colophene" to the viscid yellow oil remaining after distilling off all that is volatile in a current of steam from the crude product of the action of sulphuric acid on the hydrocarbons of the formula $C_{10}H_{16}$. The name was assigned by Deville to the portion of the product obtained from French turpentine, boiling slightly above 300°,† having the composition $C_{20}H_{32}$ (comp. Riban, *op. cit.*, p. 40); it appears desirable, however, wherever possible, to use names such as dicamphene, &c., for the polymerides of the $C_{10}H_{16}$ hydrocarbons of known composition, so as to indicate their molecular weight and origin.

Colophene from American and French turpentine cannot be distilled even under reduced pressure without undergoing decomposition, a considerable proportion of the distillate being volatile in a current of steam; in the following this volatile portion will be spoken of as the "colophene distillate." The decomposition takes place at a temperature much below the boiling point of any of the $C_{10}H_{16}$ polymerides. Thus on distilling colophene under a pressure of about 2 inches of mercury, the retort being heated in an oil-bath, regular though slow distillation took place as the temperature of the liquid rose from 155° to 185°; after this but little passed over until the temperature rose to 210° to 230°, when the $C_{10}H_{16}$ polymeride began to distil; the portion collected below 200° was almost entirely volatile in a current of steam.

* The distillate above 184° was found on analysis to contain 85·0 per cent. carbon, and 11·5 per cent. hydrogen; the amount of oxygen present is therefore considerable (3·5 per cent.).

† This product apparently was termed colophene, on account of its resemblance to the substance of high boiling point in the so-called rosin oil obtained on distilling colophony, which Deville appears to have considered identical with colophene. The two products, however, are totally different, and are readily distinguished by the remarkable property of the latter to form a grease when triturated with slaked lime. If this grease is strongly heated in a retort, the rosin oil distils over, leaving the lime almost colourless and free from carbonate.

On heating colophene, after the water which it retains has passed over* and the liquid begins to boil, some sulphur dioxide is invariably given off, notwithstanding the removal of the acid by steam-distilling the mixture of crude "terebene" and colophene in contact with alkali, and a small amount of sulphur is deposited in the condenser. Almost the whole of the products volatile in steam pass over before the non-volatile substances begin to distil. As the distillation proceeds, the boiling point rises higher and higher, and a considerable portion remains unvolatilised when the temperature almost approaches that of dull redness; the residue is either solid when cold or extremely viscid. Colophene is therefore originally a complex mixture of polymerides, some of which are of very high boiling point; or the comparatively simple polymerides of which it consists are partially converted into more complex polymerides on heating.

The colophene distillate has a pale yellow colour and a peculiar unpleasant odour which it does not lose on distillation, but which is destroyed by sodium.

If the non-volatile portion of the distillate from colophene is slowly passed through a tube heated just to visible redness it undergoes very little alteration, the product yielding scarcely any steam-distillate.

The amount of distillate obtained from colophene varies considerably in different experiments, but on the average that prepared by the action of acid varying in strength from the 2 : 1 to concentrated acid yields from 20 to 25 per cent. of its volume of steam-distillate. We have endeavoured to ascertain the conditions affecting this variation but without much success, as will be evident on comparing the results tabulated below:

* Very frequently the colophene after steam-distillation forms an emulsion from which it is almost impossible to separate the water. In this case, it should be heated in a flask on the sand-bath or over a rose burner. As a rule, it then separates after a time into two layers. The plan we have usually adopted has been to measure the wet colophene, and afterwards deduct the water which distils over. For distilling small quantities, ordinary Florence oil flasks may be employed with advantage, the flask being half charged and placed as nearly as possible on its side; a piece of tubing 3 or 4 feet long is a sufficient condenser.

Nature of Colophene.

	Percentage of distillate.
From American turpentine—	
Prepared by action of H_2SO_4 at 0°, Exp. 9, p. 737....	20·0
Obtained in preparing crude terebene, Exp. 14, p. 738	17·0
Prepared by adding H_2SO_4 at atm. temp., and allowing to cool spontaneously to 20—25° before again adding acid, Exp. 16, p. 740.....	25·1
Prepared by adding acid as in preparing crude terebene, Exp. 17, p. 740	17·8
Ditto.....	15·0
From action of 2 : 1 acid without cooling	26·1
Ditto.....	19·6
Ditto.....	24·2
Ditto.....	25·0
From action of 1 : 1 acid at about 80°, p. 741	15·2
From French turpentine—	
Prepared by action of H_2SO_4 at 0°, Exp. 10, p. 737 ..	25·0
From action of H_2SO_4, any considerable rise of temperature being prevented by keeping the vessel in cold water.....	11·0
Obtained in preparing crude terebene, Exp. 15, p. 739	11·6
From action of 2 : 1 acid without cooling	24·1
Ditto.....	23·6
Ditto.....	21·2
Ditto, but with cooling	20·6
From Exps. 1—5, p. 736, with acids of various strengths	22·5

The colophene obtained in converting the products of low activity (3—1°) from American turpentine, p. 738, gave 27·8 per cent. of distillate; that obtained in a similar manner from French turpentine, p. 739, gave 30·6 per cent. The colophene produced on heating the almost inactive product of the action of 1 : 1 acid on American turpentine until entirely deprived of its activity gave 13·2 per cent. of distillate. Colophene prepared from terpilene from terpin by the action of 2 : 1 gave only 8 per cent. of distillate, and that formed by the action of 4 : 1 acid on the terpilene isolated from crude terebene gave 8·4 per cent. The colophene from crude terebene and 2 : 1 acid furnished 13·3 per cent., that from the colophene distillate itself 16·6 per cent. A quantity of colophene formed on treating the inactive camphene obtained by the action of sodium on the solid hydrochloride from turpentine with 4 : 1 acid gave on distillation only a mere trace of substance volatile in steam.

It is difficult to formulate any very definite conclusions from these results; they appear, however, to indicate that the polymerides which are decomposed on distillation are in the main directly derived from the terpene.

The distillates from the colophene prepared by the action of acid varying in strength from the 2 : 1 to the concentrated acid were all mixed together. By treatment with 2 : 1 and subsequently with 4 : 1 sulphuric acid, it was ascertained that about 80 per cent. was convertible into substances which did not volatilise in steam; a little less than three-fourths of the remainder was cymene, slightly more than one-fourth consisting of the hydrocarbon $C_{10}H_{20}$.

Submitted to fractional distillation from sodium, the greater part was found to boil at about 156—160°, and ultimately solid inactive camphene, identical in all respects with that from crude "terebene," was obtained in quantity from these fractions.

As in the case of crude "terebene," the fraction next largest in amount was collected at about 175—180°; this consists of terpilene mixed with cymene and the hydrocarbon $C_{10}H_{20}$. Crystalline terpilene dihydrochloride was obtained from this fraction by submitting it to the treatment described on p. 746. The colophene distillate, however, contains relatively much less terpilene than crude "terebene." It is difficult to estimate the actual amounts of camphene and terpilene in either, both on account of the considerable loss which is unavoidably incurred during the prolonged fractional distillation, and on account of the impossibility of ascertaining the composition of the intermediate fractions; but apparently there is at least twice as much terpilene as camphene in crude "terebene," and less than half as much terpilene as camphene in the colophene distillate.

A very small quantity of the colophene distillate boils below 150°. This portion has a peculiar odour, recalling that of a mixture of benzene and ethaldehyde, and when treated with concentrated sulphuric acid, it forms a solution which becomes of a green colour on the addition of water. This behaviour resembles that of the lowest fraction of the distillate from the product of the oxidation of turpentine on exposure to air, and also that of an at present unknown constituent of "rosin spirit;" it is highly probable, therefore, that the substance of low boiling point in the colophene distillate is not even indirectly a product of the action of sulphuric acid, but that it is derived from the oxidation product in question.

On the first occasion of examining the colophene distillate, sodium was employed from the commencement, and the distillation continued until the temperature reached about 180°; the residue, which was considerable in amount, was mixed with water, the oil steam-distilled, and the distillate submitted to fractional distillation *per se*.

The greater part was ultimately collected at about 200° and at about 210°. The latter fraction being set aside for some weeks, deposited a quantity of crystals. These crystals were collected, pressed, dissolved in alcohol and reprecipitated by water, and were finally sublimed. The substance thus purified possessed the odour and general properties of *camphol* (borneol), with the sole exception that its alcoholic solution was inactive to polarised light; it fused at 198—199°, and boiled at 209—210°. The crystals float on water, but when compressed or fused, they give a solid cake which, when free from air, sinks in distilled water at the ordinary temperature; this is a good rough test for distinguishing camphol from camphor. On combustion with copper oxide in oxygen, this substance gave the following results:

	Subs.	CO_2.	OH_2.
I.	·1888	·5414	·1981
II.	·1886	·5376	·1996
III.	·1422	·4031	·1528

These results agree with those required for a substance of the formula $C_{10}H_{17}.OH$:

	I.	II.	III.	Mean.	Theory.
C.....	78·15	77·74	77·23	77·70	77·92
H.....	11·66	11·76	11·93	11·74	11·69

When mixed with ordinary nitric acid, it liquefied immediately; the liquid became hot and nitrous fumes were evolved. A few grams were treated with nitric acid kept cool, and after half an hour the solution was diluted with water; the precipitated substance, after purification, was found to melt at 172—173°, and to resemble common camphor, from which, however, it differs in being optically inactive.

The question arose whether the camphol thus obtained was pre-existent in the colophene distillate, or was the product of the action of the sodium on some constituent of the distillate. The colophene distillate was found on analysis to contain 85·6 per cent. carbon, and 12·1 per cent. hydrogen, and (by difference) 2·3 per cent. oxygen. To decide this, a quantity of about 2,500 c.c. of colophene distillate was fractioned entirely without the use of sodium, and finally a fraction was collected between 208° and 212°, which became nearly solid when cooled to −12° on adding a fragment of camphol. Evidence of the presence of camphol in this fraction was more readily obtained by exposing a small quantity spread over a large clock glass; after a few hours, the whole of the oily matter had evaporated, and the surface of the glass was coated with crystals.

The fraction collected at about 200° mentioned above is contaminated with camphol, of which it has the odour; for when exposed in a

thin layer to the air, it deposits a small quantity of crystals of this substance. On analysis it gives numbers near to those for camphol. Like the similar fraction obtained from crude terebene, it gives on treatment with 4 : 1 sulphuric acid and steam distillation, a small quantity of an oil which has a strong peppermint-like odour, and yields a magnificent purple colour in contact with concentrated nitric acid. It is therefore probable that the substance which is the chief constituent of this fraction, whatever its nature, is identical with that contained in the similar fraction from crude terebene, and that it has the same origin (comp. p. 746). Oxidation probably takes place not only during the fractional distillation, but also during the preparation of the colophene, when the terpene is agitated in contact with the air, usually at an elevated temperature. A considerably larger amount of substance of high boiling point is obtained from the colophene distillate than from crude terebene; this should evidently be the case if they are derived from an oxidation-product, since there is a double opportunity for oxidation to occur.

As it may appear possible that the camphol we have obtained is also formed by the decomposition of the oxidation-product so often alluded to, it should be stated that the fraction collected at about 210° of the distillate from this product does not deposit crystals when allowed to evaporate spontaneously.

A small portion of the colophene distillate does not pass over, even at 220°; but this is undoubtedly a product of oxidation formed during the fractioning, as it does not volatilise in a current of steam.

We have not yet had sufficient material at our disposal to examine the distillate from the colophene prepared from pure camphene or pure terpilene; that obtained from the latter appears to contain a relatively very large proportion of cymene and the hydrocarbon $C_{10}H_{20}$, which together constitute more than half its bulk.

§ V. *Discussion of the Results.*

Our experiments show that the action of sulphuric acid on the terpenes is to convert them partly into the isomeric optically inactive hydrocarbons camphene and terpilene, and partly into polymerides.

In as far as the formation of camphene and terpilene is concerned, the action of sulphuric acid is therefore analogous to that of hydrochloric acid, since the solid monohydrochloride obtained from the terpenes is in all probability a camphene-derivative and the dihydrochloride a terpilene-derivative. The conditions which affect the proportions in which the isomerides are produced by the action of the two reagents, are also in a measure comparable: thus, according to Berthelot (*Ann. Chim. Phys.* [3], **37**, 223), the terpene of French

turpentine is converted into (terpilene) dihydrochloride when placed in contact with aqueous hydrochloric acid, or when its solution in acetic acid, alcohol, or ether is saturated with hydrochloric acid gas, and one of us has confirmed these results (Tilden, *Deut. Chem. Ges. Ber.*, **12**, 1131; *Chem. News*, **40**, 256; comp. Flawitzky, *Deut. Chem. Gez. Ber.*, **12**, 856); our experiments indicate that under similar conditions, when weak (1 : 1) sulphuric acid is employed, the terpenes yield terpilene only. When the terpenes, however, are submitted to the direct action of hydrochloric acid gas, the solid monohydrochloride —which as we have said above is probably a camphene-derivative— is the chief product, but little (terpilene) dihydrochloride being formed (comp. Riban, *op. cit.*, p. 30), and in a similar manner, as we have shown, concentrated sulphuric acid gives rise to the formation of camphene, although in this case terpilene is also produced in considerable quantity.

The manner in which the conversion of the terpene into the isomeric camphene and terpilene takes place under the influence of the acid cannot be sufficiently discussed as long as the constitution of these hydrocarbons is unknown, as is undoubtedly the case at present. Probably it is the end result of a series of changes perhaps of an analogous character to those which may be supposed to occur in the formation of trimethylethylene, $CH(CH_3):C(CH_3)_2$, from the amylic alcohol of the formula $(CH_3)_2CH.CH_2.CH_2.OH$. Doubtless, in the first instance, combination takes place between the hydrocarbon and the acid, but the resulting compound (probably an "acid sulphate" analogous to ethyl hydrogen sulphate) is unstable, and at once breaks up, the acid being regenerated; and if it be supposed that the elements of the acid are not split off in the order in which they became associated with the hydrocarbon, and that perhaps deeper changes also take place at the moment when in consequence of the separation of the elements of the acid the molecule is in a state of unstable equilibrium, we can understand the formation on the one hand of an isomeride (terpilene) which has the same combining power as the parent hydrocarbon, and on the other of an isomeride (camphene) which has only half the combining power of the parent terpene. It is also conceivable that the changes here pictured do not affect each molecule individually, or do so only partially, but that interaction occurs between the molecules of sulphate formed by the combination of the terpene with the acid, the SO_4 or HSO_4 group of the one molecule being split off in combination with two atoms or a single atom of hydrogen of another molecule: in this case, according as the hydrocarbon residues of the two molecules remain separate or combine, so either an isomeride of the parent terpene or a polymeric hydrocarbon is produced; higher polymerides would be formed by the interaction of a greater

number of molecules of sulphate, and it is obvious that in this way several isomeric polymerides may result, since not only the sulphate from the terpene, but also those from camphene and terpilene, may take part in their formation. It is possible also that the sulphates enter into reaction with the uncombined hydrocarbons.

It should be stated that the views here enunciated have already been in part foreshadowed by Deville in the following passages:—

"Je conviendrai d'appeler camphène la base du camphre artificiel solide, et térébène celle du camphre liquide (*op. cit.*, p. 38).

"Au contact de l'essence et de l'acide il se forme un sulfate de camphène, et analogiquement avec ce qui se passe avec l'acide hydrochlorique, un sulfate du térébène, ou au moins du térébène. Il paraît que ce dernier sulfate ne peut rester dans cet état de combinaison, ou même ne peut se former, puisque aussitôt le mélange de l'acide fait celui-ci distille, et qu'il se dégage en même temps de l'acide sulfureux. Le sulfate de térébène se detruit donc, et après la dissociation des éléments, acide sulfurique et térébène, il y a altération d'une certaine quantité de celui-ci par une portion correspondante de l'acide sulfurique, donnant pour résultats de l'acide sulfureux, du soufre, de l'eau, et enfin du charbon ou un corps beaucoup plus carboné que le térébène.* Le sulfate de camphène se détruit à son tour dans les mêmes circonstances, et en donnant les mêmes produits. Seulement, comme on devait s'y attendre, ce n'est pas le camphène que l'on obtient, mais un corps isomérique avec lui et provenant d'une altération moleculaire qu'il subit, exactement comme il arrive lorsque l'on distille sur la chaux le camphre artificiel, et que l'on obtient un liquide privé de rotation et qui n'est pas le camphène" (*ibid.*, p. 68).

The production of camphol (borneol) on distilling crude colophene is highly remarkable. It is conceivable that such a body might be formed by the action of water on a sulphate derived from camphene, but in this case it should occur in the crude "terebene," and not in the colophene distillate. Very possibly its formation is connected with the evolution of a small amount of sulphur dioxide, which is almost invariably observed on distilling crude colophene.

Crude colophene is doubtless a mixture of polymeric hydrocarbons of the formula $(C_{10}H_{16})$, only the highest of which probably are decomposed on distillation. Riban has observed a similar decomposition of the solid optically active polymeride to which he assigns the formula $C_{40}H_{64}$, obtained by the action of antimony trichloride on French turpentine; this, however, yields the so-called isoterebenthene, an optically active isomeride of terpilene, and apparently no other hydrocarbon of the formula $C_{10}H_{16}$. The camphene and terpilene formed on

* This does not take place when the free sulphuric acid is removed before distilling.

distilling crude colophene may be assumed to result from the decomposition of different, perhaps isomeric, polymerides, but there is not sufficient evidence to show whether the polymeride which yields the former is directly derived from the terpene, or whether it results from the polymerisation of camphene itself; as camphene, however, appears to yield a colophene which furnishes comparatively little volatile matter on distillation, it is more probable that it is directly derived from the terpene.

Riban states that the yield of pure "terebene" (*i.e.*, nearly pure camphene) is equal to 10 per cent. of the parent terpene. It is difficult to form an accurate estimate, but our opinion is that the amount of camphene in the original steam distillate and in the colophene distillate together is certainly twice as great as this. No doubt it would be difficult to separate more than the amount stated by Riban by fractional distillation alone, but probably it will be found that considerably more may be obtained by approximately fractioning out the camphene, using sodium to destroy the small amount of oxygenated substance present, mixing the fraction collected at 156—160° with about an equal volume of alcohol, saturating with hydrochloric acid, draining the hydrochloride on a vacuum filter, &c., and finally regenerating the camphene by heating the hydrochloride with an alcoholic solution of potassium hydroxide. The decomposition of the hydrochloride takes place so readily in a closed vessel at 100—110°, that probably it will suffice to heat the mixture in a vessel attached to a condenser which is connected with a column of mercury 500—600 mm. high. We are inclined to think as the "colophene distillate" contains so much more camphene than "crude terebene," that, instead of heating the terpene until deprived of its optical activity, and then distilling, it will be advisable to entirely polymerise the terpene, and after removing the cymene by steam distillation to distil the colophene.

§ VI. *Oxidation of Camphene.*

Riban has shown that the lævorotatory camphene obtained from the monohydrochloride prepared from French turpentine is converted into lævorotatory camphor when oxidised with a mixture of potassium dichromate and sulphuric acid. We find that in like manner the inactive camphene separated either from crude "terebene" or from the colophene distillate yields inactive camphor, which in all external properties resembles ordinary camphor.*

* According to Fittig (*Deut. Chem. Ges. Ber.*, **10**, 522), "terebene" yields the same product (terpenylic acid) as ordinary turpentine or lemon oil on oxidation. Fittig does not state how the "terebene" was prepared.

Camphor thus prepared gave the following results on analysis:—

·1263 substance gave ·3660 gram CO_2 and ·1181 gram OH_2.

		Theory.
C	79·03	78·94
H	10·48	10·52

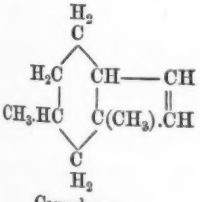
Heated for some time on the water-bath with nitric acid, this camphor is converted into camphoric acid as shown by the following analysis:

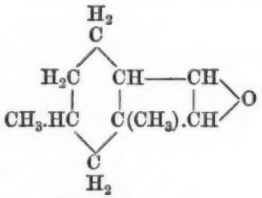
·1733 gave ·3795 CO_2 and ·1253 OH_2.

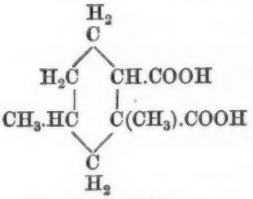
		Theory.
C	59·72	60·00
H	8·03	8·00

The acid thus prepared, however, melts at 202—203°, and the anhydride obtained by distilling it alone, and crystallising the product from a mixture of alcohol and ether, melts at 223°; the acid regenerated from this anhydride was found to melt at the same temperature as before. Riban also noticed that the melting point of the camphoric acid which he prepared was much higher (197°) than that of ordinary camphoric acid (187°).

The formulæ which one of us has suggested for camphene and camphor (Armstrong, *Deut. Chem. Ges. Ber.*, **11**, 1698) are based on the supposition that synthetical and natural camphor are, chemically speaking, identical bodies, differing only in their optical characters; but if this be the case they ought to yield acids differing only in their optical characters. It must not be forgotten, however, that the optically inactive modification formed by heating dextrocamphoric acid with hydrochloric acid (Wreden, *Liebig's Ann.*, **163**, 327) differs greatly from this latter in melting point (113°), and there is no reason to doubt its "chemical identity" with the parent acid.


Camphene.


Camphor.


Camphoric acid.

Camphene is readily oxidised by nitric acid, yielding a considerable quantity of a syrupy product, which slowly deposits crystals on standing. We intend to study this product, and also carefully to compare the behaviour generally of inactive camphor with that of ordinary camphor.

§ VII. *Summary.*

1. The action of sulphuric acid on the terpenes varies both according to the concentration of the acid and the temperature at which the action takes place.

2. The terpenes are most readily deprived of their optical activity by means of concentrated acid acting at an elevated temperature. By the action of the same acid at about 0°, they are chiefly polymerised, the rotatory power of the portion not polymerised being affected only to a comparatively slight extent.

3. Weak sulphuric acid (1 : 1) acts very slowly on the terpenes at the ordinary temperature, and tends chiefly to polymerise them. By its action at about 80°, however, they are ultimately rendered optically inactive, a considerable proportion remaining unpolymerised. Acids intermediate in concentration between 1 : 1 and undiluted acid appear to furnish intermediate results.

4. The portion of the product of the action of concentrated acid which is volatile with steam does not contain, as Deville, Riban, and Orlowski state, a liquid optically inactive isomeride, boiling at about the same temperature as the parent terpene, neither is cymene the only other constituent of this portion of the product (Riban, Orlowski). So-called terebene, in fact, does not exist, the substance described under this name being merely impure optically inactive camphene; and in the said product it is associated with terpilene, the optically inactive isomeride of the terpenes which boils at about 178°, and also with cymene and a paraffin-like hydrocarbon of the formula $C_{10}H_{20}$. Terpilene is the chief constituent of the product in question, and next in amount is camphene; the quantity of cymene is relatively small, and that of the hydrocarbon, $C_{10}H_{20}$, still smaller.

5. The similar product of the action of 1 : 1 acid at about 80° does not appear to contain any camphene, but consists principally of terpilene; it also contains cymene, the hydrocarbon $C_{10}H_{20}$, and a certain amount of oxygenated substance which is but little, if at all, affected by sodium.

6. The portion of the product of the action of sulphuric acid of whatever strength, which does not volatilise with steam—crude colophene—is probably a mixture of polymerides of the form $(C_{10}H_{16})_n$. When submitted to distillation, it yields a considerable amount of matter volatile in steam. The product examined by Deville, Riban, and probably by Orlowski, was therefore a mixture of two products.

7. The steam distillate obtained from colophene prepared by the action of acids varying in strength from the 2 : 1 to the concentrated acid resembles in composition the volatile product above described (4),

but contains a considerably larger proportion of inactive camphene; it also contains a small quantity of an optically inactive camphol (borneol).

8. The distillate from the colophene obtained by the action of 1 : 1 acid on the terpenes, and that from the colophene derived from terpilene, contains a relatively much larger amount of cymene and of the hydrocarbon $C_{10}H_{20}$ than the distillate from colophene prepared by means of stronger acid. It is doubtful whether it contains camphene.

9. The amount of distillate obtained from colophene prepared under various conditions is subject to considerable variation; the law of variation has not yet been ascertained.

10. The small amounts of substances other than those mentioned which are found in the volatile product of the action of sulphuric acid, and also in the colophene distillate are probably the result of the decomposition of a product of oxidation formed during the prolonged fractional distillation, and in the latter case also during the preparation of the colophene.

11. Probably the best method of preparing pure inactive camphene from the terpenes will be to polymerise the terpene completely by means of an excess of concentrated sulphuric acid at an elevated temperature, and having freed the colophene from cymene, &c., by steam distillation, to distil it alone, then to fraction the colophene distillate, and treat the fraction collected at about 156—160° with hydrochloric acid, and afterwards decompose the camphene hydrochloride so formed by means of an alcoholic solution of potassium hydroxide.

12. Inactive camphene is converted into inactive camphor by oxidation with a mixture of potassium dichromate and sulphuric acid. This inactive camphor yields camphoric acid on oxidation with nitric acid, but the acid prepared in this manner has a much higher melting point than ordinary camphoric acid.

We propose to continue this investigation, and also to re-examine the products of the action of other modifying agents, such as phosphoric anhydride and boron fluoride, on the terpenes.

London Institution.
Clifton College, Bristol.

LXXVI.—*A Study of Certain Cases of Isomorphism.*

By Harry Baker, Dalton Chemical Scholar in the Owens College.

Marignac has shown, in the case of the double fluorides and oxyfluorides, that the groups $M^{iv}F_4$, $M^{v}OF_3$, and $M^{vi}O_2F_2$ must be considered as isomorphous, inasmuch as they unite with alkaline and other fluorides to form double salts, which have a similar composition and an identical form. The following table exhibits the composition of some of these isomorphous salts (Marignac, *Archives d. Sciences Phys. et Nat.*, **23**, 1865) :—

$M^{iv}F_4$.			$M^{v}OF_3$.	$M^{vi}O_2F_2$.
		$3NH_4F.HF.SnF_4$	$3NH_4F.HF.NbOF_3$	
			$2NH_4F.NbOF_3$	$2NH_4F.WO_2F_2$
$2NH_4F.TiF_4.Aq.$			$2KF.NbOF_3.Aq.$	$2KF.WO_2F_2.Aq.$
$ZnF_2.TiF_4.6Aq.$	$ZnF_2.SiF_4.6Aq.$	$ZnF_2.SnF_4.6Aq.$	$ZnF_2.NbOF_3.6Aq.$	
$CuF_2.TiF_4.4Aq.$			$CuF_2.NbOF_3.4Aq.$	$CuF_2.WO_2F_2.4Aq.$

But in the series $3MF.R(OF)_4$—which should also include a uranium salt described by C. Bolton—Marignac, in order to show the analogy of their forms, assumes that bodies, although belonging to different crystallographical systems, but yet having forms similar to one another, must be considered as isomorphous. With respect to the potassium fluoxyuranate, C. Bolton states that it separates "from a hot saturated solution in crusts of small crystals, upon which larger well-built prisms are formed belonging to the monoclinic system; by spontaneous evaporation of the cold solution, there form well-built twin crystals, which belong to the tetragonal system." From this statement (*Zeitschr. f. Chemie*, 1866, 353) of the crystalline forms of this body, it must be considered as dimorphous, a property not possessed by any of the other salts of the series $3MF.R(OF)_4$. Further, the relation of the axes and the crystallographical forms of the quadratic crystals, as given in Wurtz's *Dictionaire de Chemie* (Bolton?), viz., $a : c = 1 : 2{\cdot}0815$ and the forms m $(=\infty P)$ and $p(=0P)$, exhibit no external analogy of form to the octohedron, or to the forms closely related to those of the regular system, as observed by Marignac in the salt $3NH_4F.TiF_4$. For these reasons it seemed desirable to re-examine this potassium fluoxyuranate, to decide whether it bore any crystallographical relations to the chemically corresponding salts described by Marignac, and at the same time to verify the action of the latter on polarised light.

The following list gives the composition of these salts:—

(1) $3KF.NbOF_3$.
(2) $3NH_4F.NbOF_3$.
(3) $3NH_4F.SiF_4$.
(4) $3NH_4F.ZrF_4$.
(5) $3KF.ZrF_4$.
(6) $3NH_4F.TiF_4$.
(7) $3KF.UO_2F_2$.

In describing salt No. 1, Marignac (*Archives d. Sciences Phys. et Nat.*, **23**) states:—"These crystals have exactly the appearance of cubes without any modification. But optical examination proves that they belong neither to the cubical system nor to that of the square prismatic. Besides, their angles are not exactly right angles, the determinations varying between 90° and 90° 30′, and accordingly it has been impossible for me to determine their crystalline system. I may remark that this salt, the form of which does not differ sensibly from a cube, has a formula analogous to that of the basic fluozirconate of potash (No. 5), $3KF.ZrF_4$, which crystallises in regular octohedrons, and to those of the fluosilicate and fluotitanate of ammonium (Nos. 3 and 6), $3NH_4F\ SiF_4$ and $3NH_4F.TiF_4$, the first of which crystallises in square prisms, the second in the same, or perhaps in cubes."

Respecting No. 2 we further read:—"This salt occurs in small, perfectly transparent cubes or octohedrons, or more frequently still in cubo-octohedrons. Their angles are exactly those of the regular system, and they are singly refractive. . . . . The crystalline form of this salt is exactly the same as that of the basic ammonium fluozirconate, $3NH_4F.ZrF_4$ (No. 4). It is perhaps also the same as that of basic ammonium fluotitanate (No. 6), for this salt crystallises in cubes, or in prisms closely approaching cubes. Besides, the comparison of this (No. 2) with the corresponding potash salt (No. 1) gives a new example, to add to those already known of isomorphism in two different crystallographical systems."

Potassium fluoxyniobate, $3KF.NbOF_3$. (*No.* 1).—The niobic oxide used for the preparation of this and the following salt was free from tantalum, being a portion of that prepared by Professor Roscoe from Greenland columbite for his researches on the niobium chlorides. By fusing niobic oxide with excess of acid potassium fluoride, and crystallising the fused mass from hot water, small cuboïdal crystals were obtained. The salt was analysed by gently heating with sulphuric acid and treating the residue with boiling water, when the niobic oxide remained insoluble (Marignac). 0·1884 substance gave 0·0728 Nb_2O_5 and 0·1437 K_2SO_4; and 0·3242 of another preparation gave 0·1255 Nb_2O_5 and 0·2472 K_2SO_4. These results agree with Marignac's formula, $3KF.NbOF_3$:—

	Calculated.	Found.	
Nb p. c.....	27·57	27·11	27·16
K „	34·31	34·24	34·24

The crystals, cubical or distorted to rectangular plates and prisms, examined in polarised light, were perfectly inactive, so that they must belong to the regular system, and consequently are strictly isomorphous with the following ammonium salt; this is not in accordance with Marignac's observations.

Ammonium fluoxyniobate, $3NH_4F.NbOF_3$. (*No.* 2).—This salt was prepared by dissolving hydrated niobic oxide, prepared by precipitating a solution of potassium niobate with ammonia, in hydrofluoric acid, and adding ammonium fluoride. The crystals, octohedrons and cubo-octohedrons, were inactive in polarised light. By heating 0·1894 of the salt with sulphuric acid, 0·0902 of niobium pentoxide was left, showing the crystals to contain 33·41 per cent. Nb, while the formula $3NH_4F.NbOF_3$ requires 33·83 per cent.

Ammonium fluosilicate, $3NH_4F.SiF_4$. (*No.* 3).—This was prepared by evaporating a solution of the normal octohedral ammonium fluosilicate, mixed with ammonium fluoride till crystallisation commenced. There separated long square prismatic crystals, possessing double refraction. 0·443 of this salt, after pressing between filter-paper, was dissolved in water and precipitated with barium chloride, with addition of alcohol; thus was obtained 0·755 of a mixture of barium fluoride and silicofluoride, which by ignition left 0·532 barium fluoride. These numbers give 13·61 per cent. Si and 62·75 per cent. F, while the formula requires 13·07 per cent. Si and 61·75 per cent. F.

Potassium fluozirconate, $3KF.ZrF_4$. (*No.* 5).—The zirconia used for this and the succeeding preparation was purified by converting it into the normal potassium fluozirconate, and recrystallising this. The solution of these crystals in water, mixed with potassium fluoride in excess, deposited small brilliant octohedral crystals, possessing simple refraction. 0·374 ignited with sulphuric acid left 0·4085 zirconia and potassium sulphate, which, extracted with boiling water, left 0·1296 ZrO_2, giving 25·54 per cent. Zr and 34·48 per cent. K, instead of the calculated 26·37 per cent. Zr and 34·56 per cent. K.

Ammonium fluozirconate, $3NH_4F.ZrF_4$. (*No.* 4).—A small quantity of the preceding salt was heated with sulphuric acid; and the sulphates were dissolved in water and precipitated with ammonia. The washed zirconia was dissolved in hydrofluoric acid, ammonium fluoride added, and lastly ammonia, till nearly neutral. From this solution small octohedral crystals possessing simple refraction were deposited; 0·3071 ignited with sulphuric acid left 0·1327 zirconia; *i.e.*, 31·88 per cent. Zr instead of 32·51 per cent. as required by the formula.

Ammonium fluotitanate, $3NH_4F.TiF_4$. (*No.* 6).—Metatitanic acid was prepared from rutile, and dissolved in concentrated sulphuric acid; the cold diluted solution was then precipitated with ammonia. This titanic acid was dissolved in hydrofluoric acid, and ammonium fluoride, and lastly ammonia was added till nearly neutral. This solution gently evaporated deposited crystals often dendritic, but showing rectangular faces. On polarised light they acted only slightly, the transmitted light with crossed Nicols never being brighter than a bluish-grey; with the action of a selenite film the action was more distinct, but not nearly so vivid as with the basic ammonium fluosilicate. By precipitating 0·4207 of this salt with ammonia, 0·1463 of titanic acid was obtained, equivalent to 21·71 per cent. Ti; calculated 21·12 per cent.

Potassium fluoxyuranate, $3KF.UO_2F_2$. (*No.* 7).—According to Bolton, "potassium fluoride causes in a solution of uranium nitrate a heavy crystalline lemon-yellow precipitate, which, by washing with cold water and recrystallisation from hot water, can be obtained pure. It is well in the preparation of this salt to add an excess of potassium fluoride, as the salt is soluble in uranium nitrate." By crystallising the salt thus prepared from pure water or from a solution of acid potassium fluoride (containing not more than 13 per cent.), tabular triclinic crystals are always formed. But by crystallisation from a nearly saturated solution of acid potassium fluoride, a salt separates in minute quadratic crystals. Furthermore, by adding potassium fluoride to a solution of uranium nitrate in quantity insufficient to produce a permanent precipitate, or by recrystallising either of the preceding salts from water containing a little uranium nitrate, monoclinic crystals are obtained; so that three distinct potassium fluoxyuranates exist.

A. *Quadratic potassium fluoxyuranate.*—The form of this compound varies considerably with the method of preparation. The following forms occur:—$2P\infty$; P; $\infty P\infty$; and 0P. The type is always pyramidal; single crystals (Fig. 1) $2P\infty$. $\infty P\bar{\infty}$ and P. OP subordinate. Penetration-crystals are most generally formed, the twin plane being $P\infty$; thus Fig. 2 shows a penetration-twin of $2P\infty$, and Fig. 3 a penetration trilling of $P.2P\infty$, owing to the position of the twin-plane and the length of the vertical axis being nearly unity, the P faces of the three individuals fall almost into one and the same plane; the crystals appearing as an octohedron with a re-entering angle in the centre of each edge: $b : \dot{b} = 1{\cdot}000 : 0{\cdot}992$.

		Calculated.	Found. Mean.
$2P\infty$: $2P\infty$ (terminal)	= (201) : (021)	101° 52′	101° 49′
$2P\infty$: P	= (201) : (111)	140 56	140 33
$2P\infty$: $2P\infty$ (lateral)	= (201) : (20$\bar{1}$)	126 36	126 51
$2P\infty$: $\infty P\infty$	= (201) : (100)	153 18	153 3
$2P\infty$: $2P\infty$ (summit)	= (201) : ($\bar{2}$01)	53 24	53 13
P : P (terminal)	= (111) : (1$\bar{1}$1)	109 41	109 34

The crystals are always extremely small, but have smooth and brilliant faces; in colour they are yellow, and hardly show any fluorescence. Their solubility in the mother-liquor is very small, and decreases with the amount of acid potassium fluoride present. They dissolve very slowly in cold water, but may be recrystallised unaltered from warm water. Sp. gr. at 20° is 4·263.

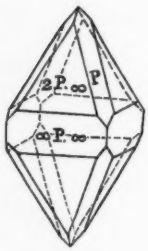


Fig. 1.

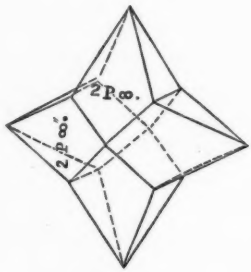


Fig. 2.

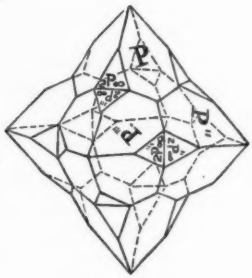


Fig. 3.

Quadratic Potassium Fluoxyuranate, $3KF.UO_2F_2$.

The method of analysis was—(1.) After removing fluorine by heating with sulphuric acid, the uranium was separated and weighed as phosphate; from the filtrate the excess of phosphoric acid was removed as ferric phosphate, and the potassium weighed as sulphate. (2.) The fluorine was precipitated as calcium fluoride after removing the uranium as ammonium uranate. The salt is perfectly anhydrous. 0·779 substance gave 0·5802 $P_2O_5.2UO_3$ and 0·4109 K_2SO_4; 1·084 substance gave 0·4315 CaF_2.

	$3KF.UO_2F_2$	Found.
K	24·24	23·68
U (= 240)	49·56	49·78
F	19·58	19·37
O	6·62	—
	100·00	

B. *Triclinic potassium fluoxyuranate.*—Although this salt may be made to yield crystals of very appreciable size, yet in almost every

case the faces give multiple images by reflection. Further, their action on polarised light shows that they almost invariably consist of several individuals interpenetrating and not always in a simple manner. For these reasons it has been impossible to make a fully satisfactory determination of the crystalline form, yet the following account may serve till better formed crystals have been obtained. A small single crystal of prismatic type (Fig. 4), perfect in its faces, afforded the following measurements, showing it to be triclinic with the following forms :—$\infty P\bar{\infty}$. (100). $\infty P\breve{\infty}$. (010). 0P (001). + P ($1\bar{1}\bar{1}$). ∞P ($1\bar{1}0$); another somewhat similar crystal contained also the forms $+\frac{1}{2}P\frac{\bar{1}'}{2}$ ($12\bar{2}$) and $+\frac{1}{2}P\frac{\bar{1}}{4}$ ($14\bar{2}$).

$$\breve{a} : \bar{b} : \dot{c} = 1{\cdot}000 : 1{\cdot}591 : 0{\cdot}904;\ \alpha = 72°\ 38';\ \beta = 116°\ 23';\ \gamma = 111°\ 57'.$$

		Calculated.	Found.
$\infty P\bar{\infty} : \infty P\breve{\infty}$	$= (100) : (010)$	101° 15′	101° 15′*
$\infty P\bar{\infty} : \infty P$	$= (100) : (1\bar{1}0)$	146 36	147 30 approx.
$\bar{\infty}P\bar{\infty}$: 0P	$= (100) : (001)$	114 48	114 48 *
$\infty P\breve{\infty}$: 0P	$= (010) : (001)$	79 25	79 25 *
$+P : \infty P\bar{\infty}$	$= (1\bar{1}\bar{1}) : (100)$	114 10	114 10 *
$+P : \infty P\breve{\infty}$	$= (1\bar{1}\bar{1}) : (010)$	99 25	99 25 *
$0P : (+P)$	$= (001) : (\bar{1}11)$	120 30	120 51
$+P : \infty P$	$= (1\bar{1}\bar{1}) : (1\bar{1}0)$	119 32	119 34
$+\frac{1}{2}P\frac{\bar{1}'}{2} : \infty P\breve{\infty}$	$= (12\bar{2}) : (010)$	134 31	133 29
$+\frac{1}{2}P\frac{\bar{1}'}{2} : +\frac{1}{2}P\frac{\bar{1}}{4}$	$= (12\bar{2}) : (14\bar{2})$	93 31	94 00 approx.
$(+\frac{1}{2}P\frac{\bar{1}'}{2}) : 0P$	$= (1\bar{2}2) : (001)$	139 23	140 00 approx.
$+\frac{1}{2}P\frac{\bar{1}'}{2} : +P$	$= (12\bar{2}) : (1\bar{1}\bar{1})$	120 54	120 20

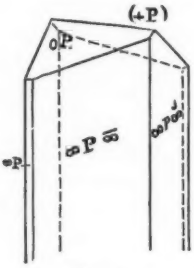


FIG. 4.

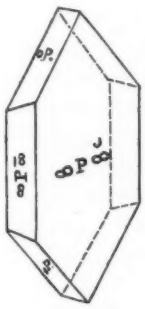


FIG. 5.

TRICLINIC POTASSIUM FLUOXYURANATE.

The general form of the crystals is, however, that of thin almost hexagonal plates, formed from the above by the predominance of the brachypinacoid (Fig. 5). These tabular crystals are in almost every case complicatedly twinned, generally interpenetrating, but sometimes

grouped into six-rayed rosettes; measurements were not possible. The crystals are perfectly stable, and may be recrystallised from pure water, or a dilute solution of acid potassium fluoride, one part dissolving at 12° in 35 parts of a 3·7 per cent. solution, and in 60·4 parts of a 7 per cent. solution. The larger crystals show a distinct fluorescence. Sp. gr. at 20° is 4·379. The uranium and potassium were separated by boiling the solution of the salt, after heating with sulphuric acid, with ammonium sulphide. The black precipitate, uranous oxide and sulphur, after filtration and washing, was dissolved in nitric acid and again precipitated with ammonium sulphide; and the precipitate dried, strongly ignited, and weighed as the black oxide, U_2O_5. The united filtrates evaporated to dryness and ignited, left the potassium as sulphate. 0·8967 substance gave 0·4177 K_2SO_4, and 0·5563 U_2O_5; 1·040 substance gave 0·399 CaF_2; 1·060 substance gave 0·3965 CaF_2, and 0·8908 substance gave 0·4156 K_2SO_4, and 0·5520 U_2O_5. The mean of a number of previous analyses on several preparations were K = 20·97 per cent., and U = 53·32 per cent., but the uranium was precipitated only once with ammonium sulphide.

	$5KF.2UO_2F_2$.	Found.	
K.....	21·49	20·91	20·95
U.....	52·73	53·18	53·10
F.....	18·75	18·67	18·20
O.....	7·03	—	—
	100·00		

The only double fluoride to which this is analogous in composition is $5NaF.2ZrF_4$, which Marignac (*Ann. Chem. Pharm.* [3], **60**, 257) has described as forming tabular monoclinic crystals. That these two salts are not isomorphous is not strange, since the potassium and sodium salts are not generally isomorphous, and also since the fluozirconates are not usually isomorphous with other chemically corresponding double fluorides.

C. *Monoclinic Potassium-fluoxyurante.*—This salt shows in a very marked degree a green fluorescence. The faces of the crystals are generally rough or slightly curved, and hence the measurements are

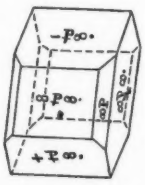


FIG. 6.—MONOCLINIC POTASSIUM FLUOXYURANATE.

only approximative. The type is horizontally prismatic through predominance of the ortho-pinacoïd and domes; forms observed—

$$\infty\breve{P}\infty \,.\, \infty\breve{P}\infty \,.\, +\breve{P}\infty \,.\, -\breve{P}\infty \,.\, \infty P. \text{ (Fig. 6).}$$

	Mean.	Probable error.
$\infty\breve{P}\infty : -\breve{P}\infty = (100) : (101)$	$= 148° 10'$	$\pm 26'$
$\infty\breve{P}\infty : +\breve{P}\infty = (100) : (10\bar{1})$	$= 125\ 47$	± 23
$\infty\breve{P}\infty : \infty P = (100) : (110)$	$= 140\ 0$	$\pm\ 7$

whence $\breve{a} : b : \dot{c} = 1{\cdot}000 : 0{\cdot}918 : 1{\cdot}065$, and $\beta = 66° 0'$.

Sp. gr. of the crystals at $20° = 4{\cdot}108$; their solution in warm water deposits them by spontaneous evaporation unaltered. It was analysed in the same manner as the previous salt. The water was estimated by ignition with lead oxide and collection in a calcium-chloride-tube. 0·625 substance gave 0·1946 K_2SO_4; the uranium was removed as phosphate; 0·5800 substance gave 0·1813 CaF_2, and 1·0458 substance gave 0·3196 CaF_2; 0·9824 substance gave 0·0427 H_2O.

Second Preparation.—0·889 substance gave 0·0383 H_2O; 0·7367 substance gave 0·5086 U_3O_8, and 0·2274 K_2SO_4; 0·8335 substance gave 0·2620 CaF_2.

	$3KF.2UO_2.F_2.2H_2O$.	Found.		
K	14·14	13·97	—	13·86
U	57·82	—	—	58·53
F	15·99	15·10	14·87	15·30
O	7·71	—	—	—
H_2O	4·34	4·35	—	4·31
	100·00			

To this salt there is no corresponding double fluoride or oxyfluoride.

From these experiments it is evident that the salt *analysed* by C. Bolton was the quadratic one, but no connection is visible between the forms here described, and the data given in Wurtz' *Dictionaire*;* and as Bolton does not state that the formula $3KF.UO_2F_2$ also belongs to the "well formed monoclinic prisms," considerable doubt may be expressed as to their composition; their method of preparation would lead one to suppose them to be the triclinic salt above described; but with the data in Wurtz' *Dictionaire*,* no analogy of form is evident.

Ammonium Fluoxyuranate.—Bolton has also described an ammonium salt, obtained "in small crystals by evaporation of a solution of

* "The monoclinic forms offer $p(=0P)$, $m(=\infty P)$, $o'(=-\breve{P}\infty)$, $a'(=+\breve{P}\infty$. Relation of the axes 1·375 : 1 : 3·477; inclination of the axes = 99° 40'. Angles $po = 77° 0'$; $pm = 82° 14'$; $ma' = 72° 50'$. In the quadratic crystals the relation of the axes is 1 : 2·0815, and the faces observed are m and p."

ammonium uranate in hydrofluoric acid, over sulphuric acid. This salt was not analysed." The resemblance in form of this salt to the quadratic potassium salt is most striking, convincing one almost of their isomorphism, and consequently of their analogous composition, and it therefore seemed desirable to determine if this be so. This salt can be best prepared in a similar way to the quadratic potassium fluoxyuranate; but a comparatively very small quantity of acid ammonium fluoride causes the precipitation of the salt from a solution of uranic nitrate, thus differing notably from the potassium salt, and probably pointing to the non-existence of ammonium salts corresponding to the triclinic and rhombic potassium fluoxyuranates. The faces of the crystals are always very rough and dull from numerous salient facets; twins like Fig. 3 are common; but they generally have 0P faces on all the terminal angles; the summit angle P : P lies between 71° and 72°, other measurements were not possible. Sp. gr. at 20° = 3·186. The fluorine was estimated as in the potassium salts, the ammonia by distillation, and the uranium by ignition, finally intense, and weighing as the black oxide U_2O_5. (1.) 0·7786 substance required 5·23 c.c. HCl (1 c.c. being equivalent to 0·01899 NH_4). (2.) 0·6414 substance left 0·4258 U_2O_5; after recrystallisation 0·2686 gram left 0·1792 U_2O_5. (3.) 0·2646 gram 0·1743 U_2O_5; and after recrystallisation 0·2843 gram left 0·1899 U_2O_5. (4.) 0·6241 gram left 0·4178 U_2O_5; 0·6611 gram gave 1·0187 $2NH_4Cl.PtCl_4$, and 0·0054 Pt; 0·6524 gram gave 0·2935 CaF_2.

	$3NH_4F.UO_2F_2$.	Found.			
U	57·02	—	56·90 57·18	56·46 57·24	57·39
NH_4..	12·86	12·75	—	—	12·56
F	22·52	—	—	—	21·90
O	7·60	—	—	—	—
	100·00				

This salt then exactly corresponds with the quadratic potassium fluoxyuranate in composition and also in form, and is consequently another member of the general group $3MF.R(OF)_4$; which we may now describe:—

	Crystallographical axes all at right angles $b : \dot{c}$.		Refraction.
(1)	$3KF.NbOF_3$	= 1·0 : 1·0	simple
(2)	$3NH_4F.NbOF_3$	= 1·0 : 1·0	simple
(3)	$3NH_4F.SiF_4$	= 1·0 : ?	double
(4)	$3NH_4F.ZrF_4$	= 1·0 : 1·0	simple
(5)	$3KF.ZrF_4$	= 1·0 : 1·0	simple
(6)	$3NH_4F.TiF_4$	= 1·0 : 1·0 (nearly)	double
(7)	$3KF.UO_2F_2$	= 1·0 : 0·992	double
and also (8)	$3NH_4F.UO_2F_2$	= 1·0 : 0·992 (approx.)	double

It is also possible that the salt $3NH_4F.WO_3$ described by Marignac (*Ann. Chim. Phys.* [3] **69**), as forming regular octohedrons, and the salt $12NH_4F.V_2O_5.2VOF_3$, which I have described (*Journ. Chem. Soc.*, 1878, vol. **33**, p. 392), as forming pyramids having nearly the angles of an octohedron, belong to this group of compounds. Their chemical analogies are indeed not evident beyond the relation of 3 : 1 existing between the ammonium and the metal present; but coupling this with the similarity of form, it will be admitted that such a connection is rendered at least probable, and that the relation would be no more profound than that between the two perfectly isomorphous salts $3NH_4F.NbOF_3$ and $3KF.ZrF_4$.

Thus with all these salts a very close *external* analogy of form exists, except with $3KF.NbOF_3$ and $3NH_4F.SiF_4$, upon which no pyramidal faces have been observed. When examined optically, however, they are found to differ, some being singly and others doubly refracting. Now Marignac has pointed out many cases in which chemically analogous compounds crystallise in forms closely resembling one another, but yet belonging to different crystallographical systems.* Further, De Senarmont (*Ann. Chim. Phys.*, 1851 [3], **33**, 391) and H. Topsöe and C. Christiansen (*Ann. Chim. Phys.* 1873 [4], **37**) have shown that among isomorphous bodies a relation between the composition crystalline form, and optical properties is not always evident. If then some chemically analogous bodies belonging to the same crystallographical system, and differing in form by only small variations of the interfacial angles, and therefore isomorphous, have optical properties differing very widely from those of each other; may we not consider other chemically analogous bodies as isomorphous, although, either by reason of the small differences between their interfacial angles, or because of the dissimilarity of their optical properties, they are placed in different crystallographical systems?

* *Ann. Min.* [5], **9**. On the iodate of ammonium and of potassium; *Ann. Min.* [5], **15**. On acid ammonium and acid potassium fluorides; *Mem. de la Soc. de phys. et d'hist. nat. de Genève*, **14**, Part I. On the chlorates of sodium and of silver; *Ann. Chim. Phys.* [3], **60**. On the basic ammonium and potassium fluozirconates, and the corresponding ammonium, titanium, and silicon fluorides; *Compt. rend. de l'Acad. d. Sciences*, **45**, 652. On the relations between the quadratic and regular systems; also *Archives d. Sciences phys. et nat.*, **23**, already quoted.

LXXVII.—*On the Transformation-products of Starch.**

By C. O'Sullivan.

Recently (*Bull. Soc. Chim.*, **30**, 54) MM. Musculus and Gruber published a paper, in which they place me amongst the adversaries of the so-called theory of the molecular splitting up of starch. They cannot have read my paper (*Chem. Soc. J.*, 1876, **2**, 125,), in which I showed that this molecular splitting up appeared to take place not according to one equation alone, but at least to three. Since the publication of that paper I have observed proportions of dextrin and maltose amongst the products of the action of malt-extract (diastase) on starch-paste, which would seem to point to a splitting up of starch according to a fourth equation, viz.:—

$$(B')-\underset{\text{Starch.}}{C_{72}H_{120}O_{60}} + 3H_2O = 3\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\alpha\text{-Dextrin-ii.}}{C_{36}H_{60}O_{30}}$$

It will be seen that this expression completes the series of which my equations (C) and (B) are the first and second members; this, which I shall call (B') equation, for the present, being the third member; and my (A) equation the fourth. Besides the proportions of maltose and dextrin derivable from starch by the action of malt-extract, of which the equations here indicated are expressions, other relative quantities of these bodies have been observed, but these are probably due, as I have already partly shown, either (*a*) to a splitting up of the starch partially according to one equation, and partially according to one or more others, or (*b*) to the action of the active agent or agents (it is possible that there are at least four of them in the cold water extract of malt) of the malt-extract employed, on the dextrin or dextrins at first produced. The proportion of maltose and dextrin represented by the equation given by MM. Musculus and Gruber for the splitting up of starch, belongs, without question, as I shall show by-and-by, to the latter class.

These authors confirm that portion of my work relating to maltose; but they have made a serious error (about 2 per cent.) in their mode of calculating the specific rotatory power (*Bull. Soc. Chim.*, **30**, 56). If maltose has an apparent specific rotatory power $[\alpha_j] = +150°$, a 1 per cent. solution of it in a 220 mm. tube does not require a compensation = 13·5°, nor even 13·5 *divisions* of a Soleil-Dubosq instrument. It is well known that if the divisions of that instrument be

* This paper was presented to the President of the Chemical Society of Paris, on the 18th June last, and extracts therefrom read to the Society on July 4th following.

calculated for the $[\alpha_j]$ line, 100 of them = 24°.* Now a solution in water of maltose containing 10 grams in 100 c.c. in a tube 1000 mm. in length, produces a rotation for the $[\alpha_j] = +150°$ or 24° : 150° : : 100 divisions : 625 divisions of the Soleil-Dubosq instrument, 1000 mm. : 220 mm. : : 625 divisions : 137·5. Hence a solution of 1 gram maltose in 100 c.c. in a 220 mm. tube gives a deviation requiring a compensation of 13·75 divisions of the scale of the instrument of Soleil-Duboscq, and not 13·5° for a 1 per cent. solution. If MM. Musculus and Gruber have employed this factor in converting their observations into normals, they must submit their work to a correction throughout, or their work does not agree with mine. Their work, even when corrected, does not agree with my already published observations on the same subject; and as the points at issue are of some technical as well as scientific importance, I may be permitted to place some recent observations made by me upon the bodies under consideration, before the Chemical Society.

Maltose.—When the process by which this body is prepared is considered, it being necessary to separate it from *the sugars* and other constituents of malt-extract soluble in alcohol on the one hand, and from dextrin and the constituents of the extract insoluble on the other, it is more or less surprising that the observations of Schulze, and of Musculus and Gruber (especially when the method of the latter is considered) upon the optical activity of this body, should agree so closely with those originally published by me. This fact notwithstanding I am, from somewhat extended observations, now inclined to think that the numbers given to express the results of the observations do not describe the true powers of maltose; that, in fact, the body examined has been more or less impure, the impurity amounting to at least 2 per cent. It is probable that the apparent specific rotatory power of maltose for the $[\alpha_j]$ lies between + 154° and + 155°, and its cupric oxide reducing power (for definition of this term, see *Chem. Soc. J.*, 1876, **2**, 130), between 62 and 63. I am engaged in purifying this body and in accurately determining these important factors. I hope to be in a position soon to communicate the results.

The Dextrins.—MM. Musculus and Gruber assert that I attributed the optical activity $[\alpha_j] = 204°$ to dextrin or the dextrins, be they obtained by the action of diastase or of acids on starch. It will be seen by reference to my paper (*Chem. Soc. J.* **2**, 10, 581) that I have stated that power to be + 212° to + 215°, with a cupric oxide reducing power varying between 0·8 and 2·2; that soluble starch had the same activity; and that the numbers were obtained for the dextrins, no matter under what conditions they were produced from starch.

* Landolt (Das optische Drehunsgvermögen organischer Substanzen, 167) makes this number 24·5°, but this does not agree with the observed facts.

These learned gentlemen point to at least three dextrins, with different optical activities and cupric oxide reducing powers. The existence of at least four distinct dextrins, as indicated by the apparent splitting-up of starch according to my four equations, is without question highly probable; but that all these dextrins, as well as soluble starch in the pure state, have the same optical activity, and that they are not reducing bodies, is beyond doubt. My recent observations on these points are as follows:—

Soluble Starch.—This body is prepared by dissolving starch-paste at 73—74° with the least possible quantity of the cold water extract of malt, previously heated to the same temperature, boiling the solution as soon as it becomes clear, filtering, and evaporating the filtrate until a slight skin begins to form on the surface; the soluble starch falls out of the liquid on cooling as a brilliant white precipitate. This is allowed to rest for a few days; it is then treated with cold water, with which it is washed well upon a filter. It is purified by dissolving it in as small a quantity of boiling water as possible, and again filtering, if necessary, using a hot-water funnel; on cooling, the soluble starch separates from the filtrate as before. The process must be repeated three or four times. Thus purified the soluble starch cannot be dried without undergoing a slight change; a portion of it seems to be converted into an insoluble modification, and a little (from 1 to 5 per cent.) into maltose and dextrin. It is fortunately not necessary to dry this body in order to determine its optical activity and reducing power if any; the quantity of it in solution can be inferred from the specific gravity of the solution—the full extent of its solubility in cold water seems to be between 2 and 3 grams per 100 c.c. Determinations of these factors for six different preparations led to numbers varying between $[\alpha_j] = +219{\cdot}5°$ and 222·0° for the apparent specific rotatory power, and 3·5 and 0·78 for the reducing power,* the higher the observed reducing power the lower the optical activity, the body reducing only 0·78 having the activity $[\alpha_j] = +220°$. It is therefore obvious that the reducing power is due to an impurity, probably maltose, and that pure soluble starch is not a body with a definite reducing power of 6, as MM. Musculus and Gruber state it to be.

The optical activities in this paper were determined with a Soleil-Duboscq saccharimeter, 100 *divisions* of the scale being taken as equal to 24° for the $[\alpha_j]$ line, and also by a Soleil-Scheibler (Schmidt and Haensch, of Berlin), 100 *divisions* of this scale being taken as equal to 38·5 for the same line.

α-Dextrin.—This is the term I apply to the dextrin giving in solution a reddish-brown colour with iodine solution. It is produced as a

* For method by which these factors were determined see *Chem. Soc. J.*, 1876, 2, 132.

rule when starch-paste is dissolved according to my (C) equation (for conditions see *Chem. Soc. J.*, 1876, **2**, 142). I believe I have observed decompositions of starch according to this equation, the products of which gave no colour, or only a trace, with iodine; but, recently, I have only been able to obtain the colour-giving products. In the preparation of this dextrin the starch-paste is dissolved as indicated above; the solution is boiled for a short time, filtered, and the filtrate evaporated to a syrup. To this the least possible quantity of alcohol is added to produce a permanent precipitate; this is allowed to settle, and the supernatant liquid decanted off. To this liquid more alcohol (sp. gr. = 0·82) is added; the precipitate produced is impure α-dextrin. The first precipitate consists chiefly of an optically inactive or slightly lævorotatory carbohydrate, an albuminoïd, and the ash-constituents of the malt-extract, with some dextrin; the second of α-dextrin, contaminated with maltose, a further quantity of the above-mentioned carbohydrate and ash. This precipitate is allowed to settle, after which the supernatant liquid is decanted off; it is then again dissolved in a little water, and alcohol again gradually added to produce a permanent precipitate; this is also to be rejected. The process is repeated several times, and then the dextrin itself precipitated, redissolved, and again precipitated at least ten times if it be desired to get anything like a pure product. The final precipitate is next dissolved in water, the solution boiled for some time to expel the alcohol, and then evaporated with continual stirring when the solution begins to thicken. By careful management in this way α-dextrin can be obtained in perfectly colourless glassy masses. I have observed that the evaporation and drying gives rise to the formation of a little maltose, 2, 3, or even 5 per cent. being produced if large bulks of the dextrin are operated with, whereby the processes are extended over a long time. Determinations of the optical activity of six carefully prepared samples of this body dried in a current of dry air at 100°, gave numbers varying between

$$[\alpha_j] = + 218{\cdot}8° \text{ and } 219{\cdot}5°,$$

with cupric oxide reducing powers equal to from 0·14 to 1·80, the higher activities being obtained for the preparations with the lower reducing powers.

We have then a body closely approaching soluble starch in optical activity; is the difference in this activity due to an essential difference in the character of the bodies, or is it due to the presence of some impurity in the α-dextrin not present in the soluble starch? Let us consider the mode of preparation. Soluble starch can be washed with water; we must employ alcohol to wash α-dextrin. From what bodies have we to separate them? We have maltose, the reducing body on the one hand; we know that it is but slightly soluble in strong alcohol,

but soluble in water; on the other we have the impurity of the starch employed, and of the transforming agent or agents, be they the cold extract of malt or prepared diastase, portion (30 to 40 per cent.) of the solid matter of the one, and the whole of the other, from its mode of preparation, being insoluble in alcohol but soluble in water. These bodies, therefore, can be separated from soluble starch; they can only be imperfectly separated from α-dextrin; they are optically inactive, or slightly lævo-rotatory, hence the difference in activity between soluble starch and α-dextrin can without hesitation be written down to these impurities. Let us consider the question further. Suppose 100 grams starch were decomposed according to my (C) equation, 82·6 grams of α-dextrin would be produced. To bring about this result a quantity of cold water extract of malt, containing 6 to 8 grams of solid matter, must be employed; this contains from 2 to 3 grams of matter insoluble in alcohol, behaving in this respect almost exactly like dextrin, and being optically totally different to that body: hence if the whole of the 82·6 grams of α-dextrin were precipitated by alcohol, a quantity of the impurity equal to from 2·5 to 3·5 per cent. would be precipitated with it; and hence if the optical activity of the α-dextrin so prepared were determined, it would of necessity be found to be at least from 2·5 to 3·5 per cent. less than the truth, say only 2 per cent.; increase 218·8 and 219·5 by 2 per cent., and we get 223·2 and 223·9, optical activities higher than were obtained for soluble starch, probably because the soluble starch is itself slightly contaminated by the optically inactive bodies, and because I have succeeded by partial precipitation in separating at least a portion of these bodies (which, by the way, I hope soon to be able to describe more fully) from the samples of α-dextrin for which the above determinations were made. I believe, therefore, I am justified in concluding that soluble starch and α-dextrin, the slight observed difference notwithstanding, have in the pure state the same optical activity, namely, a solution of 10 grams of dry body ($x C_6H_{10}O_5$) in 100 c.c., in a layer 1000 mm. in depth produces a deviation for the $[\alpha_j]$ line equal to at least 222°, that is, the apparent specific rotatory power is $[\alpha_j] = +222°$. Of course this is not an absolute value; it must, however, closely approach the truth. A moment's consideration of the above facts shows, too, that the hypothesis that soluble starch and α-dextrin have a definite reducing power of 6 cannot be maintained.

β-Dextrin or *dextrins* are the dextrin bodies distinguished by giving no colour in solution with iodine.

β-Dextrin-i.—I apply this term provisionally to the dextrin produced when starch-paste is dissolved according to my (B) equation (*Chem. Soc. J.*, 1876, **2**, 141). It is the achroodextrin-i of MM. Musculus and Gruber, who attribute to it the following powers:—

Specific rotatory power = $[\alpha_j] = 210°$
K* = 12

I have prepared this dextrin by dissolving starch-paste under the conditions necessary to produce proportions of maltose and the dextrin required by the equation indicated, and purifying the product as much as possible by the processes described above as being employed in the preparation of α-dextrin. Determination of the leading factors in six samples so prepared and purified led to the results—

$[\alpha_j] = 216{\cdot}4°$ and $217{\cdot}8°$ as extremes, with
K = 2·4 and 0·56 ,,

These numbers obtained for the optical activity are slightly lower than those obtained for soluble starch and for α-dextrin. Allowing that all three bodies have in the pure state the same optical activity, this is what should be expected. In the preparation of this body, starch yields a mixture containing only 65·46 per cent. of it, instead of 82·60 per cent., as in the case of α-dextrin; the same amount of malt-extract or of diastase must be employed, or from 25 to 40 per cent. more, and hence a quantity of optically inactive impurity, insoluble in alcohol, is introduced to bring about the transformation, equal to at least 4 or 5 per cent. of the dextrin produced. The body has to be separated from a higher proportion of maltose, and from a higher proportion of impurity closely approaching itself in its behaviour to alcohol. Hence this β-dextrin-i has *not* the powers attributed to it by MM. Musculus and Gruber, but it is highly probable that in the pure state it has the same optical activity and cupric oxide reducing power as soluble starch and α-dextrin, namely, numbers not far removed from—

$[\alpha_j] = + 220°$
K = 0·00

β-Dextrin-ii.—I apply this term to the dextrin produced when starch-paste is dissolved according to my (B′) equation. I prepared and purified it as far as possible by the methods already described in the purification of α-dextrin. On drying it in a current of dry air at 100°, I found the following factors for it, four different preparations being examined:—

$[\alpha_j] = 216{\cdot}0°$ to $217{\cdot}5°$
K = 3·0 to 0·6

numbers not far removed from those obtained for β-dextrin-i; hence what has been said with regard to that dextrin must be said of this one: it has the same rotatory power in the pure state, and has in all probability no action on cupric oxide solution.

* I suggest this symbol K for the cupric oxide reducing power.

β-Dextrin-iii is the dextrin produced when starch-paste is split up according to my (A) equation (*Chem. Soc. J.*, 1876, **2**, 136). It corresponds exactly with the achroodextrin-ii of MM. Musculus and Gruber; they, however, bring about the decomposition of starch in its production in a manner which is not scientific. They mix diastase solution (*Bull. Soc. Chim.*, **30**, 62) with starch and cold water, heat the mixture at first to 76°, and then, after cooling, maintain the temperature at 50—60° for an hour. Starch is dissolved by diastase at the temperature of its gelatinisation, or a few degrees below that point. These gentlemen no doubt employed potato starch (pure?), and as this starch gelatinises below 63—64°, it would be dissolved below that temperature: hence there was no necessity to heat it to 76°, nor to maintain the temperature at 50 to 60° for an hour; the transformation or splitting would have been complete in a few minutes—ten at the outside after the gelatinisation of the starch—and the same proportion of maltose and dextrin produced as was obtained by them. They observed a reducing power equal to 45 for the bodies in solution from the starch; the theoretical number required by my (A) equation is 44·1. I have prepared this dextrin from the products of the splitting up of starch according to (A) equation, and purified it by partial fermentation (*having previously boiled* the products of the decomposition), and afterwards by repeated partial and complete precipitations with alcohol in the same manner as α-dextrin was purified. The partial precipitations are more necessary in the case of this dextrin than in that of either of the dextrins above mentioned; firstly, because it constitutes only 32·12 per cent. of the products of the transformation of starch—the bodies of the malt-extract or diastase, insoluble in alcohol, employed in producing the transformation, thereby amounting to from 8 to 12 per cent. on it; and secondly, because the yeast employed in the fermentation by which portion of the maltose is eliminated yields to the solution 2 or 3 per cent. more on the dextrin of impurity insoluble in alcohol, raising the total impurity of this character to from 10 to 15 per cent. of the dextrin to be purified. Indeed, the purification of β-dextrin-iii from all this impurity is an exceedingly difficult task, and one not so easily accomplished as MM. Musculus and Gruber seem to think. I have determined the leading factors for several preparations of this body, carefully purified as much as possible from the mucilage of the yeast and of the malt-extract, and obtained the following results:—

$$[\alpha_j] = + 215° \text{ to } 217°$$
$$K = 2·5 \text{ to } 0·6$$

These numbers are sufficiently close to those obtained for soluble starch and the other dextrins, to leave little doubt that the optical

activity of this body and its action on copper solution are the same as the other bodies mentioned, and not a body having

$$[\alpha_j] = 199^\circ \text{ and}$$
$$K = 12,$$

as MM. Musculus and Gruber assert.

β-Dextrin-iv (?) *or the achroodextrin*-iii *of MM. Musculus and Gruber.*—I have not followed these gentlemen in their mode of bringing about the transformation of starch to obtain the products containing this dextrin; it is sufficiently easy to arrange the relative quantity of starch and malt-extract or diastase, and, as I have elsewhere shown, the *time* and temperature, to obtain products from starch having a reducing power of 52. The products can be obtained in a few hours; it is not necessary to employ five days in obtaining them. These products are not due to the *splitting up* of starch alone; they are due in part to the action of the active agents upon the transformed bodies. Products from starch, with a reducing power of 51—52°, by the action of malt-extract, are sufficiently common, especially when the starch is dissolved at first at the high temperatures, the temperature lowered, a fresh quantity of malt-extract added, and the digestion then carried on for some time below 60°.

I isolated this dextrin from the product of the transformation of starch, having a reducing power of 52, and containing, therefore, not more than 22 per cent. dextrin. It was purified in the same way as the dextrin last mentioned. Dried in a current of dry air at 100°, it gave—

$$[\alpha_j] = 212^\circ \text{ to } 214{\cdot}7^\circ, \text{ and}$$
$$K = 2{\cdot}8 \text{ to } 0{\cdot}7.$$

The optical activity is lower somewhat than that observed for the other dextrins; but then it must be remembered that the impurities insoluble in alcohol, from which it must be separated, amount to at least 20 per cent. of itself. It is no easy matter to effect this separation, nor even to purify the body as far as I have done; indeed, I have not as yet been able to obtain any sample absolutely free from bodies containing nitrogen, and from ash: hence the low optical activity, and hence I feel justified in concluding that this body in the pure state has the same optical activity and same relation to cupric oxide as the other dextrins above described. It is no doubt sufficiently easy to obtain a body from the residue of the fermentation of the products from starch having K = 52, with the powers

$$[\alpha_j] = 190^\circ$$
$$K = 12,$$

attributed by MM. Musculus and Gruber to this body; but then it is quite as easy to show that such a body consists of an optically inactive

non-reducing body, an active reducing one, a nitrogenous one, ash, and a dextrin (β-dextrin-iv), which I shall show later is in reality identical with β-dextrin-iii above described.

Achroodextrin-γ.—Of this supposed dextrin I shall not at present say much. All the dextrins above mentioned are absolutely non-fermentable by *Saccharomyces cerevisiæ* (high fermentation yeast) alone; they yield alcohol &c., rapidly, however, in presence of *yeast* and *active diastase*—the cold water extract of malt. This is a curious fact; the malt-extract alone does not hydrate the low dextrins in the cold, yeast does not act upon them, but the two together give rise to fermentation, and consequently hydration must previously take place. Boiled malt-extract has not this effect. I may state, too, that maltose is difficultly fermentable by *Sacch. cer.*, and that its complete fermentation is an operation requiring much care and management; more, indeed, even than cane-sugar, which Pasteur in the beginning of his investigations considered not capable of complete fermentation by yeast. As in the case of cane-sugar, the fermentation of maltose at times stops dead when 50 or 60 per cent. of it is fermented; the addition of the least trace of active diastase again sets up the action with full vigour, and it then continues to the end, the whole of the maltose or cane-sugar, as the case may be, disappearing. This is the great difficulty to be contended against in separating the dextrins from the reducing body; moreover, maltose cannot be completely fermented in presence of dextrin. M. Musculus states that his achroodextrin-γ constitutes from 12 to 15 per cent. of the commercial glucoses. In analyses of some of these products published (*Jour. Soc. Arts*, **24**, 410), I pointed out the presence of what I called, for the time being, *neutral carbohydrates;* these bodies are optically inactive, and are totally different in character and composition from any of the dextrins. They are not fermentable in presence of *yeast and active diastase;* hence I am inclined to think that the said achroodextrin is a mixture of those bodies, dextrose, maltose, and one or more of the dextrins with a little ash. I have reason to look upon the neutral carbohydrates mentioned as more hydrated even than dextrose.

So much for the work relating to the dextrins. I shall in the next part consider the theoretical aspect of the splitting up or transformation of starch.

The Action of Malt-extract on the Transformed Products.

A consideration of the proportions of maltose produced from starch by the action of malt-extract, indicated above, and described in detail in the paper therein quoted, would seem to point to the conclusion that the starch-molecule is at least $C_{72}H_{120}O_{60}$, and that the production

of the four definite different proportions of maltose may be represented by the four following equations, viz. :—

$$\text{(C)}\quad \underset{\text{Starch.}}{C_{72}H_{120}O_{60}} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\alpha\text{-Dextrin.}}{C_{60}H_{100}O_{50}}$$

$$\text{(B)}\quad C_{72}H_{120}O_{60} + 2H_2O = 2C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-i.}}{C_{48}H_{80}O_{40}}$$

$$\text{(B')}\quad C_{72}H_{120}O_{60} + 3H_2O = 3C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-ii.}}{C_{36}H_{60}O_{30}}$$

$$\text{(A)}\quad C_{72}H_{120}O_{60} + 4H_2O = 4C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-iii.}}{C_{24}H_{40}O_{20}}$$

the final product undergoing the change

$$\underset{\beta\text{-Dextrin-iv.}}{C_{24}H_{40}O_{20}} + 2H_2O = 2C_{12}H_{22}O_{11}$$

slowly and gradually, and not almost instantaneously, as in the case with the change represented by the four first equations, in which the starch-paste, or the products therefrom, seem to act as a whole—the results indicated, as stated elsewhere, being obtained in the space of five minutes, or thereabouts.

It may, too, be taken that the following equations represent what takes place, and these would appear to be the more probable, as α-dextrin seems to be invariably, or almost so, formed first:—

$$\text{(C)}\quad \underset{\text{Starch.}}{C_{72}H_{120}O_{60}} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\alpha\text{-Dextrin.}}{C_{60}H_{100}O_{50}}$$

$$\text{(B)}\quad \underset{\alpha\text{-Dextrin.}}{C_{60}H_{100}O_{50}} + C_{12}H_{22}O_{11} + H_2O = 2C_{12}H_{22}O_{11} + \underset{\beta\text{-Dextrin-i.}}{C_{48}H_{80}O_{40}}$$

and so on; the starch-molecule, being broken down, yields first maltose and α-dextrin; this latter breaks down into maltose and β-dextrin-i, which in its turn splits up into maltose and β-dextrin-ii, and so on; maltose and a dextrin of lower molecular weight being produced at each step. Although the proportions of maltose and dextrins observed can be accounted for by either of these series of equations, we have at present no further proof that either in any way represents what takes place than this, that the amounts of maltose and dextrin required by them are observed under the *conditions* mentioned in my paper quoted above, but as I have therein stated, other proportions, variously intermediate, can be obtained by *altering* the conditions. In that paper the equations employed, as will be seen, were not intended as the expression of a theory, they were simply meant to represent the quantities of maltose and dextrin observed, and to indicate their origin: I had cause even then to be doubtful of the

spliting up theory, or that starch and the dextrins were polymerides. If these equations represent what really takes place, it is obvious that—

α-Dextrin must be capable of yielding, under certain easily indicated conditions, at least three different definite proportions of maltose, of which the equations, $C_{60}H_{100}O_{50} + H_2O = C_{12}H_{22}O_{11} + C_{48}H_{80}O_{40}$, would represent the first; $C_{48}H_{80}O_{40} + C_{12}H_{22}O_{11} + H_2O = 2C_{12}H_{22}O_{11} + C_{36}H_{60}O_{30}$, the second; and so on;

β-dextrin-i should yield, under conditions capable of being similarly indicated, at least two definite different proportions of maltose;

β-Dextrin-ii should yield at least one definite proportion of maltose; and

β-Dextrin-iii no absolutely definite proportion of that body; and even if it were found that the proportions here indicated were observed, it would not follow as an absolute certainty that the theory represented by the equations was the true one.

As already stated I prepared each of these dextrins and another probable one, namely, the dextrin eliminated when the proportion of maltose amongst the transformed products is equal to 85 per cent., or thereabouts, and which would probably be $C_{12}H_{20}O_{10}$, in a fairly pure state. The study of the action of malt-extract upon them then presented no great difficulty; the method of investigation, and the mode of estimating the maltose and the dextrins being the same as that described (*Chem. Soc. J.*, 1876, **2**, 125) in dealing with starch, except that the more recently observed factors for these bodies were employed. I need not go into details here: reference to the paper quoted will show how all the estimations and calculations have been made. The results obtained may be summarised as follows:—

α-Dextrin is but slightly acted upon by malt-extract at 69—70°; (*a*) at 66—70° it yields 17·4 per cent. of maltose, or thereabouts, in four to ten minutes, there being no increase in the quantity even after two hours' digestion at the same temperature, if the malt-extract be not in large excess, and this applies in all cases; (*b*) at 65—66°, 34·5 per cent. of maltose is found amongst the products of the transformation in the same time, and further digestion, at the same temperature, produces little or no increase in that quantity; (*c*) at 63—64°, 51·2 per cent. of maltose is observed; and at (*d*) below 62°, the product of the change can be made to contain 67·8 per cent. of that body, which proportion increases but gradually after the first 15 to 20 minutes, but at this temperature, with a quantity of malt-extract equal to 13 per cent. of the α-dextrin taken, I have observed, after 17 hours' digestion, 90 per cent. repeatedly, and even as much as 95 per cent. maltose, calculated upon the K determined, *dextrin constituting the remainder of the products according to the optical activity*. If these numbers be compared

with those observed for the maltose amongst the products of the transformation of starch itself, under similar conditions, it will be observed that they exactly agree one with the other. If the change from starch to α-dextrin were such as is indicated by equation (C), this dextrin ($C_{60}H_{100}O_{50}$) should yield, under the conditions mentioned, (*a*) no change; (*b*) 20·8 per cent. maltose; (*c*) 41·3 per cent.; and (*d*) 61·3 per cent. of that body, amongst the products of the splitting-up. I have before me the tabulated results of at least forty experiments and careful determinations, and I can state that the latter quantities are never observed amongst the products of a definite change, the former ones, on the contrary, almost invariably.

β-Dextrin-i, when exposed to the action of malt-extract at 66°, undergoes little change in from 10 to 15 minutes; at 63—64°, products containing 34·6 per cent. of maltose are obtained; at 62—61°, we get the same results; at 58—59°, for 15 minutes or more, little or no change in the composition of the products is observed; and, even by continuing the digestion for twice the time, and by increasing the proportion of malt-extract to twice the original quantity, the composition of the transformed products is but slightly altered. If equation (B) represented what takes place in the production of the quantity of maltose represented by it, the dextrin, β-dextrin-i, produced at the same time should behave towards malt-extract as follows:—(*a*) and (*b*) no change, (*c*) products should be obtained containing 26 per cent. maltose ($C_{48}H_{80}O_{40} + H_2O = C_{12}H_{22}O_{11} + C_{36}H_{60}O_{30}$), and (*d*) 57·2 per cent. ($C_{36}H_{60}O_{30} + C_{12}H_{22}O_{11} + H_2O = 2C_{12}H_{22}O_{11} + C_{24}H_{40}O_{20}$). These numbers are not observed, whilst products containing 34·6 maltose, or thereabouts, are almost invariably to be met with.

β-Dextrin-ii behaves like β-dextrin-i. In this case, the equation represents the quantity of maltose observed.

$$C_{36}H_{60}O_{30} + H_2O = C_{12}H_{22}O_{11} + C_{24}H_{40}O_{20}$$

requires 34·6 per cent. of maltose. In consequence of this circumstance it may be supposed that the β-dextrin-i, with which the results described above were obtained, was in reality the dextrin of the (B′) equation, or that being the (B) equation dextrin, it underwent a change in the process of isolation and purification. The dextrin was beyond all question, to begin with, the dextrin of the (B) equation, but it is no easy matter to put it beyond all doubt that no change had taken place in the process of purification. I may, however, state that three samples, prepared from three separate (B) equation products, yielded the same results. A study of the action of malt-extract upon the products of the (B) and (B′) equations would seem to indicate, however, that β-dextrin-i and β-dextrin-ii do not behave in exactly the same way, and that they are consequently not identical.

β-Dextrin-iii, the dextrin of the (A) equation, when submitted to the action of malt-extract at either of the temperatures above mentioned, yields no definite constant quantity or quantities of maltose, the increase in the reducing power of the products in the solution being slow and gradual. I have, with a quantity of malt-extract containing solid matter equal to 10 per cent. of the dextrin employed, at a temperature of 60°, observed 5, 7, 8, 10, and up to 90—92 per cent. of maltose amongst the products; the latter proportion being due to 15 hours' digestion, the former to 20 minutes' contact, and the intermediate quantities to intermediate times. A less quantity of malt-extract produces little or no change, even if the digestion be continued for hours. If this dextrin were to split up into a lower dextrin ($C_{12}H_{20}O_{10}$) and maltose, it should yield, as a definite result, products containing 51·2 per cent. of the latter body.

β-Dextrin-iv (?)—the dextrin obtained from the products of the transformation of starch and of the other dextrins, when the reducing power of these products = 52—53 (85 per cent. maltose)—behaves, when treated with malt-extract, exactly in the same way as β-dextrin-iii.

These facts, namely, that α-dextrin behaves like starch itself, and consequently cannot have a smaller molecular weight; that β-dextrin of the (B) equation and β-dextrin of the (B′) equation appear to act in the same way when isolated, although differently when in solution with the products formed at the same time; that the β-dextrin of the (A) equation and the dextrin of the products containing as much as 85 per cent. maltose, do not differ in their behaviour towards malt-extract; and that, when an action takes place with starch or any of these dextrins, the whole of the body in solution is affected at the same time, would seem to indicate that the production of maltose from starch and the dextrins is not due to a breaking-down of the molecules. The facts, however, leave little doubt that, besides α-dextrin, there are at least two, probably three, β-dextrins amongst the transformed products, the whole being capable of indication as follows:—

	α-dextrin	the dextrin of	the C equation
(? i)	β-dextrin-i	,,	of the B ,,
	β-dextrin-ii	,,	of the B′ ,,
and	β-dextrin-iii (? ii)	,,	of the A ,,

and of all the products from starch having a higher K than that required by the last equation.

At present it is rather doubtful whether we have sufficient data upon which to start a theory, even in so far only as would be an attempt to explain the changes taking place in the starch-molecule; we certainly can form no idea of the power by which that molecule is

affected. M. Musculus observed that the products of the action of diastase upon starch had a reducing power of 51, and upon *this fact* started the theory that starch split up into one molecule of *dextrose* and one of dextrin. The value of this theory can be estimated by the value that can be attributed to the interpretation of the fact upon which it is founded. The amount of weight also to be given to the theory may be easily gauged by the facts advanced in the recent papers of M. Musculus in support of it. Even the proportion of maltose and dextrin required by the equation employed by him to represent the final splitting-up, is found only amongst the products of the transformation after long digestion, and cannot, therefore, be looked upon as the result of a direct splitting-up at all.

The proportions of maltose observed by me can, as I have said, be no doubt accounted for by the equations; but, as I have shown above, the theory of which they are the expressions, namely, the breaking down of the starch-molecule into dextrin-molecules becoming smaller at each step, a molecule of maltose being formed at the same time, is not supported by all the facts described. Moreover, it is difficult to imagine two bodies like starch and the probable final dextrin, the one having a molecule six times as heavy as the other and yet both having, as I have found, the same specific gravity; and further, that the two dextrins, with identical apparent properties, should have molecules in the one three or four times as heavy as in the other. Continual work with these bodies forces the conclusion upon me that we have not, in this case, to do with a series of polymerides, but rather with a series of bodies of the same molecular weight, in which the difference in their behaviour to the agent under consideration must be accounted for by a difference of *relation in the arrangement of the molecules to one another, probably in solution alone.* We may take it that the molecule of soluble starch, or the dextrin giving a purple with iodine (we need not speculate on starch itself at present, for those bodies are formed from starch-paste without any simultaneous production of maltose) is simply $C_{12}H_{20}O_{10}$, but that these molecules in solution are arranged in groups of six sixes, all the groups being in an *intimate state of tension* one with another, so that the motion affecting one, under certain conditions, affects all under the same condition. Thus when α-dextrin is produced from starch, one-sixth of the carbon atoms appearing at the same time as maltose, each group is acted upon, six of the molecules in each group of sixes being hydrated to maltose, the remainder of the molecules in the groups again rearranging themselves in groups of six sixes for α-dextrin. It will be observed that this supposed mode of action does not symmetrically affect the groups, and it would be a consequent inference that the amount of maltose required by the theory would not be observed with any degree of sharpness. This is

so in practice; the amount of maltose required by the (C) equation cannot be constantly accurately obtained. When the groups of sixes are attacked, as is the case in the production of the amount of maltose required by the (B) equation, one-third of the carbon at once appears as maltose, the groups, moving through the α-dextrin arrangement being symmetrically attacked, yield the comparatively stable body β-dextrin-i, in which the molecules are arranged in groups of three or of four. Of four, when one of the molecules in each group is susceptible of hydration to produce, with that already in solution, the proportion of maltose required by the (B′) equation; of three, when isolated and only a third of the molecules susceptible of being acted upon; it is in this case the same as the dextrin of the (B′) equation. To produce the (B′) equation the groups of four are not symmetrically attacked, but when the change required by the (A) equation pertains, the movement of the molecules is symmetrical: hence the proportion of the maltose required by the (B′) equation cannot be obtained with as fine definition as that required by the (B) and (A) equation. This also is the case in practice. In the (A) equation dextrin the molecules are arranged in groups of two, the groups being independent one of the other, and that dextrin is consequently no longer capable of acting as a whole, and therefore of yielding a definite quantity of maltose; but, on the contrary, it yields products having a continually gradually increasing reducing power.

The theory of splitting-up and breaking-down of the starch-molecule as represented by the equations does not hold all the facts eliminated, and is not in accord with some of them; this theory, the arrangement of the molecules in groups, all dependent one on the other, and capable therefore of undergoing a simultaneous change, or being moved at once, and the rearrangement of these groups attendant upon the hydration of a definite proportion of the molecules in each of them, holds all the facts at present known—is in perfect accord with all of them: hence I am inclined to give up the former theory in favour of the latter. I do not mean to insist upon the adoption of it at present, but I am convinced it is a step in the right direction, and the working out of the problems involved in it will lead to important results, important not alone as regards this group of bodies, but as regards the light they will let in on changes of a similar kind connected with unorganised ferments. I was at first doubtful as to the advisability of advancing this theory, contenting myself with the statement of the facts, pointing out wherein they agreed with, and differed from, the splitting-up theory; but, on consideration, I thought it better to enunciate it, as I considered that the questioning of it might lead to good work in other hands. Something more is to be done chemically on the subject, but the physics of the changes must now be investigated.

The heat absorbed or eliminated during the different transformations must be determined: we can only then have an idea of the character of the apparent work done. When starch is transformed according to the proportion exhibited by the (C) equation, there is a considerable absorption of heat; this is, no doubt, the resultant of at least two changes, the solution of the starch, and the transformation of the soluble starch; how much belongs to one and how much to the other remains to be determined. I cannot say that I can continue the work in this direction, but I am still engaged upon what can further be done chemically, and I hope in a short time to add some more facts.

In conclusion, I need hardly say that the experiments and determinations upon which the statements made in this paper are based were exceedingly numerous, and could not all have been done by myself; I have, therefore, to thank my brother James for much assistance in carrying out the work.

LXXVIII.—*On a New Method of Determining Sulphur in Coal.*

By Teikichi Nakamura, Student of the Imperial College of Engineering (Kobudaigakko), Tôkiô, Japan.

The amount of sulphur in coal, a most important material in the present manufacturing world, so greatly affects its value, as to make important any improvement in the method of its estimation, and to lead me to hope, therefore, that the following note, which contains an account of what I find to be a simpler process than any other accurate one usually practised, may receive the attention of chemists.

I shall first describe my experience in trying some methods in common use.

Oxidation by means of Nitric Acid and Potassium Chlorate.

Only rarely have I succeeded in oxidising coal by this method, so far as not to leave undissolved much insoluble resinous matter rich in sulphur, and even when I have succeeded in dissolving most of the coal, the addition of water has caused a bulky precipitate of organic matter. If the whole of such a product be evaporated to dryness and heated, deflagration takes place. To prevent this, the liquid must first be evaporated with excess of hydrochloric acid; but then, on heating the dried mass, charring takes place. By protracted heating,

indeed, the carbon can be burnt off, but at the expense of the dish, which becomes much corroded by the alkaline salt, and often cracks.

A modification of this method, which proved more satisfactory, was, after treating the coal with nitric acid and chlorate, to evaporate nearly to dryness, then add fuming nitric acid, and again evaporate. By repeating this treatment with nitric acid twice more, then evaporating twice with hydrochloric acid, and finally adding water, I obtained all the sulphur in solution as sulphate. But the method is tedious, and needs an unusual degree of purity in the reagents, on account of the large quantities of them required. Besides, there is the impossibility of precipitating the sulphuric acid free from iron. The tartaric acid method is only partly successful. Boiling the precipitate with sulphurous acid and very dilute hydrochloric acid is better, but still not altogether satisfactory; so that there remains only the method by fusing the barium sulphate with alkali carbonate and reprecipitating the sulphuric acid.

Liebig's or the Potassium Hydrate Method.

This gives correct results, but is somewhat difficult to manage, in consequence of the frothing, which is generally excessive. It requires, in fact, some skill to avoid loss of substance. I fused only a little potassium nitrate with the caustic potash at first, and added more gradually to the fused mass afterwards, because if much potassium nitrate be present in the mixture at a time, too energetic an action sometimes takes place, and a slight smoke is given off. It seems to me to be the object of this method to oxidise coal slowly by potassium nitrate in potassium hydrate, the duty of the moisture being to make the action gradual. But the disadvantage due to the presence of moisture is the frothing, which becomes more violent the greater the amount of it. Besides those above mentioned, the disadvantages of this method are its wanting constant attention during the operation, the necessary addition of potassium nitrate in some excess, which afterwards interferes in the precipitation of the sulphate, and the necessity of a capacious silver dish, which is not always in the hands of the analyst.

Fusion with Alkali Carbonates and Nitre.

Without the addition of much sodium chloride, as usually practised, I have found it impossible to heat coal with nitre and alkali carbonates in such a way as to avoid deflagration. But when sodium chloride is used, which must be taken in large quantity, it becomes difficult to precipitate the sulphate afterwards. The precipi-

tation of a little sulphate is very liable to be missed, and when all is precipitated by long standing in a warm place, it carries down with it, as is well known, a quantity of other salts, which it is troublesome to wash out perfectly. Besides, it is difficult to get sodium chloride so pure that 20 grams of it, which is the amount usually taken to 1 gram of coal, shall not yield any sulphate, and as the mixture necessarily becomes very bulky, a thorough mixing and other details of treatment also become difficult to carry out.

A New Method.

The following method, which differs in principle from any methods hitherto practised, has proved in my hands very satisfactory. It consists in heating the coal below a red heat in contact with alkaline carbonates, by which the coal, whether bituminous or not, rapidly undergoes, without evolution of smoke, complete atmospheric oxidation in a manner hardly to have been expected. The details of the method are as follows. Take three or four parts of the mixed alkali carbonates, or of sodium carbonate, to one part of coal in very fine powder. Intimately mix in a large platinum dish or crucible with a dry glass rod, and heat the mixture in the dish or crucible loosely covered, at first so gently as not to volatilise hydrocarbons, that is, so that no smell or only a very faint aromatic odour is observable, a matter much more easy of execution than might be supposed. Use an argand spirit lamp instead of a Bunsen's burner, to avoid possible absorption of sulphur from the flame of coal gas. Keep at a low temperature for some time; then raise the heat by slow degrees without letting it reach that of visible redness, until the surface, which is at first of a dark grey colour, becomes only faintly grey. No smoke or odorous gases should escape during the whole of the oxidation. When the surface becomes only faintly grey, raise the temperature to a faint red heat, and keep it stationary for about forty to sixty minutes, at the end of which time the mass will become almost perfectly white, or reddish if the coal contains iron, from the complete combustion of the coal. The mass is then treated with water, filtered, and the sulphate is determined in the filtrate as usual after acidification.

To succeed in the complete oxidation of coal by this method, it is most important to pulverise it as fine as possible. The best plan is to sift it through cotton cloth. If the pulverisation be not complete, some particles of coal may remain unoxidised. When the experimenter fears this to be the case, the whole may be fused, a very little nitre added, and the remaining operation conducted as above. But it is very undesirable to fuse and add nitre, as when alkali is fused it is

very apt to come out of the vessel along the side, and nitrate interferes much with the proper precipitation of sulphate.

Some of the advantages of the new method are the sharp separation which it effects between oxide of iron and sulphuric acid, the need of only a small number and quantity of reagents compared with those required by other methods, and exceeding simplicity of management with a little skill.

To compare the results obtained by this method with those obtained by others, I have made the following determinations:—

By the nitric acid and potassium chlorate process modified as already described, a sample of coal gave 4·97 per cent. of sulphur on the first trial, and 5·10 per cent. on the second. By Liebig's process, as already described, the sample gave 4·74 per cent. By the new method, two determinations gave 4·71 and 4·60 per cent. respectively.

Of these results, those of the chlorate process are somewhat higher, but I found that my nitric acid contained traces of sulphuric acid. By testing it, simply as it was, sulphuric acid could hardly be detected, but after evaporating a good deal of it to a small bulk, and testing it after dilution, I got a distinct reaction of sulphate. Except for this, the results of the three methods agree nearly enough.

To test the correctness of the new method in another way, the following experiments have also been made.

Pyrites and galena mixed with coal, all of known composition, were roasted as described; but to insure complete oxidation of the sulphur in the sulphides, the whole was fused, a little nitre added, and then the sulphur was determined as usual. ·5445 gram of coal already found to contain ·00419 gram sulphur, and ·4015 pyrites found to contain ·19794 gram sulphur, mixed together, and tested as above described, gave 21·30 per cent. instead of 21·37. ·6255 gram coal formerly found to contain ·00477 gram sulphur and ·6330 gram galena found to contain ·08476 gram sulphur, mixed together and tested as above, gave 7·12 per cent. instead of 7·11 per cent. Another similar experiment with galena gave 6·65 per cent. instead of 6·44 per cent. These experiments show decisively that no sulphur is lost during the roasting.

It is rather remarkable that coal, and even coke, is burned completely at so low a temperature. Alkali carbonates seem, however, to have no chemical action, but to act simply mechanically, the spaces between the particles of the carbonates acting as chimneys, the oxygen wanted being of course taken from the air. The combustion travels from the surface towards the bottom.

Stirring the mixture during the oxidation impedes the process instead of hastening it, probably by closing the passages left by the consumed coal. The alkali carbonate, unchanged to sulphate, remains unaltered, as long as the mixture is not fused.

As regards the vessel to be employed for roasting, a platinum basin or crucible (better the former) is to be preferred to one of porcelain, as the action takes place much more quickly in the former than in the latter.

A current of oxygen was tried and found to hasten the oxidation a little, but the slight advantage it had did not seem worth the trouble incurred in using it, and the care requisite to prevent too violent an action. By simple roasting in the air, I can finish the oxidation in an hour and a-half.

In concluding the paper, I have to offer my best thanks to Dr. Divers, Professor of Chemistry in the Imperial College of Engineering, Tôkiô, for his valuable advice to me in working out this paper.

NOTE BY EDWARD DIVERS.—The publication of this paper is made a considerable time after it has been worked out, roughly drafted, and placed in my hands by Mr. Nakamura. In the interval, the process contained in it has been practised in the laboratory of the College and found to be very satisfactory. My object, however, in appending this note is not so much to mention this, but to point out that it was after the above paper had been completed, as above stated, that we received in the *Chemical News* for January 17th an account of Mr. Pattinson's process for determining sulphur in coal, which is somewhat similar to Mr. Nakamura's. Mr. Pattinson heats the coal to redness in a muffle with calcium hydrate, and then dissolves in hydrochloric acid. This process seems to me less advantageous than the one now published.

LXXIX. *The Bromine Derivatives of β-Naphthol.*

By ALFRED J. SMITH, B.Sc.

β-MONOBROMONAPHTHOL is obtained in the following way. The quantities of β-naphthol and bromine calculated from the following equation are weighed out:—

$$C_{10}H_7OH + Br_2 = HBr + C_{10}H_6\begin{cases} Br \\ OH \end{cases}.$$

The β-naphthol is dissolved in glacial acetic acid so as to form a tolerably concentrated solution, and the bromine is mixed with about an equal volume of glacial acetic acid. The solution of β-naphthol is first allowed to cool completely, and the flask immersed in a basin of water, while the bromine is added drop by drop from a dropping funnel, the flask containing the naphthol being shaken after each

addition. The bromine is quickly absorbed, and on standing colourless needles with an adamantine lustre crystallise out. After a few crystallisations, these become quite white and pure, and are then washed from excess of acetic acid with water, and dried between filter paper. The following are the results of the analysis of this substance.

(1.) 0·2410 of the substance gave 0·0785 H_2O and 0·4740 CO_2, which corresponds with—

	Percentage found.	Calculated for $C_{10}H_6BrOH$.
Carbon	53·65	53·88
Hydrogen	3·60	3·14

(2.) 0·2100 gave 0·0585 H_2O and 0·4145 CO_2.

	Found.	Calculated.
Carbon	53·81	53·88
Hydrogen	3·09	3·14

(3.) 0·2995 gave 0·2220 AgBr, and 0·0172 Ag.

	Found.	Calculated.
Bromine.....	35·79	35·78

β-Monobromonaphthol is soluble in alcohol, ether, petroleum-spirit, and benzene. It melts at 84°; if it is heated higher, at about 130° it begins to decompose, giving off fumes of hydrobromic acid, which at higher temperatures become very copious. If it is heated as long as fumes of hydrobromic acid are given off, a black resinous mass is left behind, and a very small quantity of crystalline sublimate is formed in the upper part of the tube. If it is mixed with excess of potash or soda and a small quantity of water in a flask, and heated in an oil-bath, first gradually to dryness, and then to 250°, a black mass is obtained, which dissolves when boiled with water; the solution thus formed is precipitated by hydrochloric acid. The precipitate thus obtained, when dried, gives on heating a sublimate of crystals of β-naphthol.

When it is oxidised by an alkaline solution of potassium permanganate at the heat of the water-bath, orthophthalic acid is formed. The β-monobromonaphthol is dissolved in the cold in a solution of caustic potash, a little solid potassium permanganate added, and the mixture is heated on the water-bath for about ten minutes. If the colour given to the solution by the permanganate is then quite taken away, more is added, and the heating is repeated; this is done till the colour of the permanganate remains after heating. Then ferrous sulphate is added and the mixture heated after the addition, and this is done till the colour of the permanganate is taken away. Hydrochloric acid is

added till the solution is acid, and then it is extracted with ether. The ethereal solution is separated by means of a tap-funnel; and on standing, a crystalline mass is deposited from it; on heating this (after drying), colourless needles of phthalic anhydride are sublimed. The melting point is 128°.

It contains no bromine, which is shown by heating it with sodium in a tube, then dissolving the mass in water, and adding nitric acid and silver nitrate, when no precipitate is formed. It is also shown to be phthalic anhydride by heating with resorcin and then dissolving in ammonia, when the yellow solution with green fluorescence, due to fluorescine, is formed.

β-Tetrabromonaphthol, $C_{10}H_3Br_4OH$, is obtained in the following manner. β-Naphthol is dissolved in glacial acetic acid and bromine is added until it ceases to be absorbed. In order to see that enough bromine has been added, it is allowed to stand for a day, and then a small quantity of the solution is added to a solution of potassium iodide and shaken up with carbon bisulphide. If the carbon bisulphide is coloured violet with iodine, it shows that enough bromine has been added, as the unabsorbed bromine sets the iodine free. The following reaction takes place:—

$$C_{10}H_7OH + 8Br = 4HBr + C_{10}H_3Br_4OH.$$

The tetrabromonaphthol soon crystallises out, forming a mass of white needles, which is filtered off from the mother-liquor by means of the Bunsen-pump, and washed from excess of bromine with glacial acetic acid, small quantities being used at a time. Then it is recrystallised from glacial acetic acid until it is quite white, when it has a constant melting point (156°). It is then washed from acetic acid with distilled water, and dried with filtering paper.

The following are the results of the analysis of this substance:—

(1.) 0·1950 gave 0·2670 AgBr and 0·0310 Ag.

	Found.	Calculated.
Bromine	69·12	69·56

(2.) 0·2440 gave 0·0235 H_2O and 0·2385 CO_2.

	Found.	Calculated.
Hydrogen	1·06	0·87
Carbon	26·63	26·09

The tetrabromonaphthol is not so soluble in acetic acid as the monobromonaphthol. It is also soluble in carbon bisulphide, benzene, and alkalis.

I also studied the effects of the oxidation of β-tetrabromonaphthol

with potassium permanganate. The process was carried on in exactly the same way as with the monobromo-compound, as described above. The ethereal extract deposited, on standing, a crystalline mass, which on heating (after drying) gave a sublimate of colourless needles. This was tested qualitatively for bromine. A small quantity of the substance was placed in a narrow tube, closed at one end, and a small piece of metallic sodium a little higher up; the tube was heated just above the sodium, which melted and ran down on to the substance, decomposing it, and forming sodium bromide. The hot part of the tube was then put into cold water, when it immediately cracked, and the water came in contact with the fused mass.

The solution gave the reaction for bromine with silver nitrate and nitric acid.

Two combustions gave the following results:—

(1.) 0·2100 gave 0·0335 H_2O and 0·3230 CO_2.

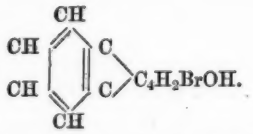
(2.) 0·2140 gave 0·0350 H_2O and 0·3280 CO_2.

	Percentage composition. (1.)	(2.)	Calculated.
C	41·90	41·77	42·29
H	1·76	1·82	1·32

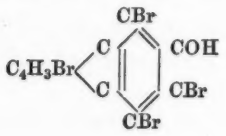
These results agree with the formula $C_8H_3BrO_3$ (the anhydride of monobromophthalic acid).

The melting point was found to be 125.°

The formation of phthalic anhydride from the monobromo-compound, and of monobromophthalic anhydride from the tetrabromo-compound, gives some insight into the constitution of these bodies. Thus it shows that in the monobromo-derivative the bromine and hydroxyl are contained in the same benzene nucleus, as shown in the following formula, as in that case only is the formation of phthalic acid possible:—



And it shows that in the tetrabromo-naphthol one benzene nucleus contains three bromine atoms and the hydroxyl, while the other contains one bromine atom, as shown in the following formula, as in that case only the formation of monobromophthalic anhydride is possible:—



β-Monobromonaphthol dissolves quietly in fuming nitric acid. On adding the solution to excess of water, a yellow resinous precipitate is formed, from which I was unable to obtain a crystallised substance. I was also unable to get a crystallised nitro-compound by adding nitric acid (both strong and dilute) drop by drop to acetic acid and alcoholic solutions of the monobromo-derivative.

This research was carried on in the University of Zürich, under the supervision of Professor Merz.

LXXX.—*The Action of Phosgene on Ammonia.*

By H. J. H. Fenton, B.A., University Laboratory, Cambridge.

When phosgene and ammonia gases, both in the dry state, are mixed together, a white neutral amorphous substance is produced, which was formerly considered to be a true compound of these bodies. Phosgene in fact was supposed to be a kind of acid ("chlorocarbonic acid"), which neutralised the ammonia, forming a salt with it.

Regnault, however (*Ann. Chim. Phys.*, **69**), showed that in reality this substance is a mixture of ammonium chloride with a body having the composition of urea. Being unable to obtain a precipitate with strong nitric acid, even in a concentrated solution of it, he concluded that the white mass contained no urea, but isomeric carbamide.

Natanson (*Ann. Chem. Pharm.*, **98**, 287) afterwards repeated these experiments with some modifications, and succeeded in obtaining a precipitate with nitric acid characteristic of nitrate of urea. He attributes Regnault's failure to do so to his gases having been insufficiently dried, which would largely increase the proportion of ammonium chloride in the mixture. Bouchardat (*Compt. rend.*, **69**, 961) has recently studied the same reaction, and finds that, in addition to the above substances, guanidine, cyanuric acid, and ammelide are produced.

No experiments were made, however, by any of these authors bearing upon the constitution of the urea or carbamide produced, and this point being of some importance, I determined to compare the properties of this substance more closely with those of ordinary urea.

Accordingly I prepared a considerable quantity of the white mixture by bringing together in large dry flasks, ammonia and phosgene gases, both thoroughly dried. The latter was obtained by Hofmann's

method, namely, by passing carbon monoxide into boiling antimony pentachloride, the resulting gas being purified from chlorine by means of metallic antimony. This process was found to be the most convenient, as the supply of gas could be easily regulated. A special arrangement was used in order to prevent stoppage of the tubes with the white solid, which at first was a serious inconvenience.

A portion of the substance thus obtained was treated in the manner described by Bouchardat, which consists in removing ammonium chloride as far as possible by repeated extraction with absolute alcohol and evaporation, digesting an aqueous solution of the alcoholic extract with silver sulphate, evaporating, and taking up with alcohol.

The portion insoluble in alcohol is treated with a slight excess of baryta-water, brought to ebullition, and a current of carbon dioxide is passed through the solution. After filtration the solution is evaporated to drive off traces of ammonium carbonate, exactly neutralised with dilute sulphuric acid, concentrated, and excess of absolute alcohol is added. By these means a crystalline deposit of guanidine sulphate is obtained.

The presence of guanidine was confirmed in this way by examination of the crystals so obtained under the microscope, and comparison with those of pure guanidine sulphate. The quantity obtained, however, was too small for analysis.

Another portion of the original white substance was evaporated to dryness with excess of barium hydrate in a vacuum over strong sulphuric acid, as suggested by Natanson.

The residue was extracted with absolute alcohol, the solution evaporated to dryness on a water-bath, the residue dissolved in water, a current of carbon dioxide passed, the solution evaporated, and the residue again digested with absolute alcohol. These latter operations were performed in order to insure the removal of traces of barium and of guanidine.

The alcoholic extract gave on evaporation crystals having all the appearance of ordinary urea. These were dried and examined in various ways.

(1.) In a former paper (*Chem. Soc. J.*, 1878, **33**, 30) it was shown that ordinary urea behaves differently when subjected to the actions of hypobromites and of hypochlorites, evolving nearly the whole of its nitrogen with the former, and only one-half with the latter, provided an excess of caustic alkali be present. The remaining half of the nitrogen exists in solution, in all probability in the form of a cyanate.

It occurred to me, therefore, that a comparison of the actions of these reagents would go a long way to prove the identity or non-identity of the above substance with ordinary urea.

Weighed quantities of the dried crystals were therefore dissolved in water, and treated with sodium hypobromite and hypochlorite in the manner previously described (*loc. cit.*).

0·0631 gram acted upon in this way by sodium hypobromite, gave 20·8 c.c. N (corr.), and

0·0588 gram gave, with sodium hypochlorite, 10·9 c.c. N, theory indicating 23·53 c.c. and 21·93 c.c. respectively for the whole of the nitrogen in urea.

The residue from this last operation gave the reactions of a cyanate when treated in the manner previously described.

(2.) A solution of the substance evaporated to a small bulk with excess of silver nitrate, gave on cooling the characteristic crystalline precipitate of silver cyanate.

(3.) A portion of the dry substance heated in a test-tube, gave off much ammonia, and the residue dissolved in water showed, when tested with potash and a drop of copper sulphate, a strongly marked biuret reaction (Hofmann, *Deut. Chem. Ges. Ber.*, **4**, 262).

(4.) A small quantity of the perfectly neutral solution of the substance heated to about 40°, with a trace of "urea ferment," in a few minutes turned decidedly alkaline, and gave off an ammoniacal odour (Musculus, *Compt. rend.*, **68**, 132).

(5.) Nitric acid and mercuric nitrate both gave their characteristic reactions of urea.

There appears, therefore, not to be any doubt as to the identity of this body with ordinary urea.

It struck me that possibly this urea might be the result of the transformation of a less stable *carbamide* during evaporation, &c. I therefore compared the actions of sodium hypobromite and hypochlorite directly upon the original white mixture.

It was previously pointed out that the quantities of nitrogen given off by the action of these two reagents are approximately the same in the case of ammonia salts, and of guanidine (*Chem. Soc. J.*, 1879, **35**, 12), and they would probably be so with symmetrical carbamide, $CO\begin{matrix}NH_2\\NH_2\end{matrix}$, whereas in the case of ordinary urea, the hypochlorite only evolves one-half. In this way it is possible, within certain limits, to estimate urea in the presence of ammonia salts.

Now the original white mixture always gave results considerably higher with the hypobromite, thus:

·070	gram	with NaBrO	evolved	17·2	c.c. N =	30·75 per cent.
·0542	„	„		13·3	„ =	30·72 „
·1211	„	NaClO	evolved	25·2	„ =	26·04 „
·0560	„	„		11·2	„ =	52·03 „

corresponding to an excess of about 20 per cent. of the total nitrogen evolved by the hypobromite.

The residue from the action of hypochlorites on the mixture also gave decided proof of the presence of a cyanate.

Ordinary urea was, therefore, in all probability present in the original substance.

From these results it is evident, either that carbamide and urea are identical, or, which seems to me more probable, that true symmetrical carbamide, $CO\begin{matrix}NH_2\\NH_2\end{matrix}$, has not been obtained, at any rate by this method. For although this method of formation would be expected to give a symmetrical body, yet it must be remembered that the reaction is not a simple one, and that the urea is always found in smaller proportion than is required by the equation:

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl,$$

and may be the result of secondary reactions.

LXXXI.—*Rehydration of Metallic Oxides.*

By Charles F. Cross.

The anhydrous basic metallic oxides, prepared by heating the precipitated hydrates, have been long recognised as hygroscopic; that they should take up water from a moist atmosphere in a definite molecular ratio, though perhaps to be predicted, is a point which appears never to have been made the subject of an experimental investigation. By exposing a number of these oxides, after depriving them, wholly or partially, of their water of hydration, to an atmosphere saturated with aqueous vapour at ordinary temperatures, I have found that rehydration occurs, attended in most cases by contraction of the reacting molecules, and therefore probably with evolution of heat, up to a definite limit of a molecular character. I take this opportunity of laying before the Society a brief account of the results which I have thus far obtained, reserving a fuller publication of the numbers which they express and other details, until I shall have completed a more extended series.

Cobalt I.—*α*. The hydrated sesquioxide was prepared by oxidising the precipitated protoxide, suspended in potash, by a current of chlorine gas. After drying at 100°, till its weight was constant, it lost on

carefully heating to a temperature below red heat, 14·69 per cent. ($2Co_2O_3.3H_2O$ contains 14·02 per cent. H_2O). The oxide, dried at 100°, was placed over water under a bell-jar, and the percentage gain of water was estimated as under:—

After a lapse of 2 days ..	29·7	per cent.	($Co_2O_3.4H_2O$ = 30·3)	
„ 4 „ ..	33·3	„		
„ 6 „ ..	34·4	„	($Co_2O_3.5H_2O$ = 35·1)	
„ 10 „ ..	35·0	„		
„ 17 „ ..	34·2	„		

There is thus evidence of the attainment of a limit, about which there is a tendency to slight variation.

(β.) The anhydrous oxide, from the above determinations, was then exposed to similar conditions, and the following numbers observed:—

After a lapse of 3 days ..	17·1	per cent.	($Co_2O_3.2H_2O$ = 17·8)
„ 7 „ ..	20·3	„	
„ 17 „ ..	25·5	„	($Co_2O_3 3H_2O$ = 26·99)
„ 21 „ ..	25·44	„	
„ 24 „ ..	24·6	„	

The limit is approximately $Co_2O_3.3H_2O$.

(γ.) The oxide was returned a second time, and the following observed:—

After a lapse of 7 days ..	17·4	per cent.	($Co_2O_3.2H_2O$ = 17·8)
„ 15 „ ..	21·03	„	($2Co_2O_3.5H_2O$ = 21·3)
„ 22 „ ..	21 9	„	
„ 30 „ ..	21·4	„	
„ 39 „ ..	20·6	„	

II. Anhydrous Co_3O_4, prepared from cobaltous nitrate by ignition, gave the following results:—*

	(*a.*) Per cent.	(*b.*) Per cent.	
After a lapse of 4 days ..	6·27	—	
„ 7 „ ..	—	7·49	
„ 9 „ ..	—	7·72	
„ 10 „ ..	10·18	—	($2.Co_3O_4 3H_2O$ = 10·09)
„ 14 „ ..	9·2	9·15	
„ 16 „ ..	9·96	—	
„ 24 „ ..	—	10·28	

I give the numbers observed in the above instances as a typical selection, but I refrain altogether from any discussion of them at the present time, and also from giving those relating to the volumes of the rehydrates.

Chromium.†—(α.) Precipitated oxide dried at 100° ($Cr_2O_3.4H_2O$ obs.),

* Rammelsberg. † Compare *Miller's Chemistry*, 2, 603 (4th edition).

became constant on exposure to rehydrating conditions, at $Cr_2O_3.7H_2O$. Observations were made upon this *rehydrate*, which is a perfectly free powder, dry to the touch, to determine the retentive capacity of the rehydrates for combined water. For this purpose the percentage of water was determined after exposure to the comparatively dry atmosphere of the balance case, with the following results :—

Observed under rehydrating conditions, and expressing the limit $Cr_2O_3.7H_2O$ (calc. 45·1 per cent.)		Then exposed in balance case.	
After 4 days	44·8 per cent.	1 hour	43·87 per cent.
„ 6 „	44·8 „	18 hours ..	43·9 „
„ 11 „	44·43 „	66 „ ..	43·89 „
„ 17 „	45·1 „		

(β.) The sesquioxide after ignition approximated to the limit of rehydration, $Cr_2O_3.3H_2O$.

Aluminium.—(α.) Oxide precipitated by boiling the solution of the ordinary hydrate in excess of ammonia; after dehydration at a low red heat, it became, on exposure to rehydration, $Al_2O_3.3H_2O$. This same limit was observed in three several instances.

(β.) The ordinary precipitated oxide, after ignition, underwent definite rehydration to $Al_2O_3.2H_2O$. After strong blowpipe ignition, the rehydration became irregular in character, approximating to the limit, $Al_2O_3.H_2O$.

Iron.—(α.) Precipitated oxide dried at 100° ($Fe_2O_3.H_2O$ obs.), approximated to the limit $Fe_2O_3.5H_2O$, and (β) after ignition to $Fe_2O_3.3H_2O$.

The rehydration of the above oxides is in all cases attended by contraction.

Copper.—Cupric oxide was investigated in three different forms:—

(α.) Oxide prepared by igniting the metal in oxygen. After six days' exposure the oxide lost 0·36 per cent. on ignition; it may therefore be regarded as permanently anhydrous.

(β.) From ignition of cupric nitrate. This takes up 2—4 per cent., but exhibits irregularity; the more usual limit is $8CuO.H_2O$.

(γ.) From sulphate by precipitation. After drying at 100° ($4CuO.H_2O$ obs.) it took up water, on exposure, in a manner which points to rehydration per saltum,* thus in 24 hours 18·8 per cent. ($CuO.H_2O = 18·4$), and in 48 hours 25 per cent. ($2CuO.3H_2O = 25·3$); it then approximated slowly to the limit $CuO.2H_2O$. After ignition

* The solution of the dynamical part of the problem I hope to effect by means of a specially constructed balance, the pointer recording the motions of the beam on a travelling surface.

it exhibited a much more tardy rehydration, becoming $CuO.H_2O$ after 37 days' exposure.

The rehydration of this oxide appears to be attended by no change of volume, so that from the observed specific gravity the percentage of water in a rehydrate may be directly calculated.

The *rehydration of anhydrous salts* also appears to be a molecular phenomenon, similar in character to that of the oxides. I subjoin the numbers observed in the case of anhydrous copper sulphate:—

	Per cent.	
After 18 hours' exposure	16·51	
„ 66 „	24·29	
„ 90 „	29·45	
„ 114 „	34·21	
„ 138 „	35·6	
„ 162 „	35·85	$CuSO_4.5H_2O = 36·07$ p. c.
„ 210 „	36·10	
„ 258 „	35·99	

The above instances suffice to explain the nature of this investigation, and the general character of the results.

LXXXII.—*Alizarin-blue.*

By G. Auerbach.

About a year and a half ago a blue colouring matter was brought into the market, intended to replace indigo generally for printing colours, and said to possess the same resistance against chlorine, sunlight, &c., as indigo itself. This colour, called "alizarin-blue," consisted of a derivative of mononitroalizarin. The expectations raised by this new dye-stuff have not been fulfilled, partly on account of its high price, and partly because it has but little power of resisting the action of sunlight. At the present time this colour has disappeared from the market, and is replaced by a much faster and more splendid colour, the so-called "methylene-blue," which resists not only sunlight, but also alkalis and acids, and dyes cotton without a mordant.

The following researches on alizarin-blue were completed in May, 1878, but have not yet been published.

The first notice about the reaction of glycerin upon phenols in presence of sulphuric acid was given by Reichl (*Berl. Ber.*, **9**, 1429), who obtained by this reaction a red colouring matter; he promised further communications about this matter, which, however, have not yet

appeared. Prud'homme afterwards treated alizarin and mononitroalizarin (as he says, in the form of a paste) with glycerin and sulphuric acid, and obtained from alizarin a colouring matter, which closely resembles alizarin itself, but whose solution in alkali is said to be orange-coloured, and to exhibit dichroism on addition of alcohol, being red-violet by transmitted and green by reflected light. From mononitroalizarin he obtained a colour which dyed iron mordants like indigo (*Bull. Soc. Chim.*, 1877, **28**, 62; *Chem. Soc. J.*, **181**, 78). Shortly afterwards Brunk made a communication to the *Soc. Ind. de Muhlhouse*, in which he stated that he had succeeded, following Prud'homme's directions, in separating from the melt of mononitroalizarin with glycerin and sulphuric acid, a blue dye-stuff, which he called *alizarin-blue*. Subsequently Graebe, Witz, and Kopp made several communications about this new colouring matter, and Graebe published his researches, especially about the base which is obtained when alizarin-blue is heated with zinc powder. The constitution of alizarin-blue has not yet been made out; Prud'homme merely says that the body is perhaps a glyceride, and Liebermann believes it to be an azo-compound.

Prud'homme's method of preparing alizarin-blue yields merely traces of this colouring matter; better results are obtained when perfectly dry mononitroalizarin is used, 1 part of mononitroalizarin, 5 parts of concentrated sulphuric acid, and $1\frac{1}{2}$ parts of glycerin, sp. gr. 1·262, being mixed and gently heated. The reaction commences at about 107° C., becomes very violent, and the temperature rises to about 200°. The mixture froths very much for a few minutes, giving off sulphurous acid and acrolëin, but settles down very soon, and then dissolves in diluted soda-lye with a bluish-green colour. The whole mass is now poured in water, boiled up and filtered; the residue is well boiled three or four times with very dilute sulphuric acid; and the filtrates are mixed together and allowed to cool, whereupon the alizarin-blue separates in brown crystals. The latter are collected on a filter, and washed with water till neutral. These brown crystals become blue during washing, the cause of this change of colour being that the blue crystallises from the acid solution with 1 mol. of sulphuric acid, which, however, is at once removed by washing with water.

For further purification the crude alizarin-blue is mixed with water, and so much borax added, that the solution becomes brownish-violet, whilst the blue, combining with the boric acid, forms a blue insoluble residue. This residue is filtered off and washed with water, till the latter shows a blue colour. By decomposing the blue residue with an acid, the blue is obtained as a violet, silky paste. To obtain it perfectly pure, it must be submitted to several crystallisations. Alcohol is a bad solvent; better are amyl alcohol, glacial acetic acid, and high-

boiling naphtha. Graebe says that the blue becomes altered by boiling with glacial acetic acid, but this is a mistake. The blue leaflets which are obtained are nothing but a compound of the blue with 1 mol. of acetic acid (calculated acetic acid 16·99 per cent., found 17·1 per cent.). This crystallacetic acid may either be removed by washing the compound with water, or by drying it at 140°. To get the blue in a pure state, it is best to use the different solvents, one after the other, and to remove the naphtha by washing with alcohol and ether. If the blue is afterwards dried at 100°, it does not lose weight, even if heated to a higher temperature.

The anthracene-blue thus obtained forms brown shining needles, often a centimeter in length, which melt at 268—270°. When heated it gives brownish-orange fumes, which condense to blue flocks, but a great part of it carbonises.

The analysis of anthracene-blue gave the following results:—

1.	Substance = 0·503 gram	H_2O	= 0·1485 gram	= 0·0165 H	= 3·28 per cent.	H.
		CO_2	= 1·2895 „	= 0·3517 C	= 69·9 „	C.
2.	„ = 0·4585 „	H_2O	= 0·1280 „	= 0·01422 H	= 3·101 „	H.
		CO_2	= 1·1635 „	= 0·3173 C	= 69·22 „	C.
3.	„ = 0·3375 „	H_2O	= 0·096 „	= 0·01066 H	= 3·158 „	H.
		CO_2	= 0·861 „	= 0·2348 C	= 69·59 „	C.
4.	„ = 0·435 „	Platin	= 0·1352 „	= 0·01916 N	= 4·404 „	N.
5.	„ = 0·5285 „	„	= 0·1772 „	= 0·0251 N	= 4·75 „	N.

By comparing those results we obtain the following figures:—

	I.	II.	III.	IV.	V.	Average.
C =	69·9	69·22	69·59	—	—	69·58
H =	3·28	3·101	3·158	—	—	3·179
N =	—	—	—	4·404	4·75	4·577
O =	—	—	—	—	—	—

The formula $C_{17}H_{11}NO_4$ requires—

C = 69·6
H = 3·70
N = 4·77
O = 21·8

The formula $C_{17}H_{10}NO_4$ requires—

C = 69·86
H = 3·42
N = 4·79

The formula $C_{17}H_9NO_4$ requires—

C = 70·1
H = 3·09
N = 4·8

It is somewhat difficult to decide between these three formulæ, but although I found the amount of hydrogen lower than that required by the first, I am on the whole inclined to adopt this formula, especially as it is corroborated by the analysis of the acetyl-compound.

0·2045 gram of the acetyl-compound gave—

H_2O = 0·0735 gram = 0·008166 H = 3·99 per cent.
CO_2 = 0·5025 „ = 0·13704 C = 67·01 „

The formula $C_{17}H_9NO_4(C_2H_3O)_2$ requires—

C = 66·84 per cent.
H = 3·98 „

Moreover the blue crystallising with 1 mol. of acetic acid requires 16·99 per cent. acetic acid, whilst 17·1 per cent. were obtained.

The analysis of several of the salts of alizarin-blue was not very satisfying, because it is very difficult to obtain these salts in the pure state. To prepare the baryta salt the blue was dissolved in ammonia, filtered, and evaporated to dryness to remove all excess of ammonia. It was then re-dissolved in water, and boiled with barium chloride. The baryta salt thus obtained gave on analysis 19·37 per cent. Ba, whilst the salt $(C_{17}H_{10}NO_4)_2Ba$ requires 19·0 per cent. Ba. But it is also possible that in the evaporation one hydroxyl has been replaced by the group NH_2, producing a body of the formula $C_{17}H_{12}N_2O_3$, whose baryta salt requires 19·05 per cent. Ba. In another experiment the blue was dissolved in caustic potash, the solution filtered, and the filtrate exactly neutralised with barium chloride; the baryta found was, however, much higher than the calculated amount, being 37·3 per cent., whilst $C_{17}H_9BaNO_4$ requires only 32·0 per cent. Ba.

Similar unsatisfactory results were obtained with the copper salt, which was obtained by dissolving the blue in concentrated sulphuric acid, filtering this solution through asbestos and pouring in a boiling solution of copper sulphate. The salt was purified by boiling with diluted acid, alkali, and water till neutral.

Its analysis gave the following results:—

				p.c.	
1. Cu salt = 0·1935 gr.	CuO = 0·0220 gr.	= 0·01756 gr.	Cu = 9·02 p.c.	H_2O = 3·27
2. „ = 0·816	„ = 0·0900 „	= 0·07186	„ = 8·805 „	„ = 3·66
3. „ = 0·888	„ = 0·1187 „	= 0·09478	„ = 10·6 „	„ = 2·85

$(C_{17}H_{10}NO_4)_2Cu + H_2O$ requires.	Found average.
Cu = 9·79 per cent.	9·475 per cent.
H_2O = 2·75 „	3·260 „

As above mentioned, alizarin-blue crystallised from naphtha forms brownish needles; by slow evaporation of a solution in amyl alcohol, it may be obtained in shining prisms often a centimeter long. In alkali,

not in excess, it dissolves with a blue colour; a larger quantity of alkali precipitates it in green flocks. On boiling the alkaline solution with zinc-dust, a red solution is formed, which when shaken with air, becomes green again, and deposits green flocks. With nitric acid it forms phthalic acid; the same acid is also formed when the anthracene-blue is heated with sulphuric acid to 230°, or when a boiling alcoholic solution of the blue is treated with nitrous acid. A cold alcoholic solution is not attacked by nitrous acid.

When the blue is heated in sealed tubes with caustic potash to 180°, it forms a white mass. On opening the tube, no pressure can be observed, and if the contents are boiled with water they turn green again. Hydrochloric acid does not alter the blue even at 260°, and baryta-water does not act upon it at to 215°. In sulphuric acid solution it is not attacked by arsenic acid.

When it is heated with sulphuric acid, phthalic acid sublimes out of the solution, and the latter on addition of caustic potash becomes brownish. It was diluted with water, neutralised with lime, filtered, and the solution of the lime salt decomposed by carbonate of soda. The solution of the soda salt was evaporated to dryness and fused with caustic potash. In decomposing the solution of the melt, hydrocyanic acid was evolved, which could also be ascertained by the Prussian blue reaction. When the solution was shaken with ether, the latter left on evaporation a small quantity of a brown substance which became violet with ferric chloride, and brownish-red with sulphuric acid and potassium nitrite.

When the blue is dissolved in glacial acetic acid and bromine is added to the solution, a yellowish-brown solution is obtained, which when neutralised with soda gives off bromine in abundance, and at the same time deposits white flocks, melting at 153°. But when these white flocks are recrystallised from benzene, light yellow crystals are obtained, which melt at 276° and exhibit all the properties of anthraquinone. Very interesting is the reaction of the bromine on anthracene-blue in the dry state. If the blue is mixed with bromine and the excess of bromine evaporated, a brown mass is formed, which is scarcely soluble in cold water; and the clear yellowish solution when heated, suddenly deposits a white precipitate, which shortly after turns blue, and dissolves to a violet-red solution, from which blue flocks separate on cooling.

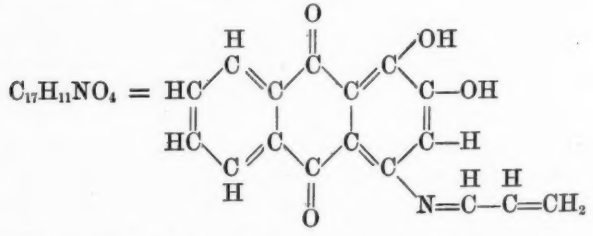
Chlorine does not act upon the dry blue when cold, but very easily if it is dissolved in nitrobenzene. The solution is separated by alcohol, and the precipitate recrystallised from glacial acetic acid. This solution yields white plates which melt at 174°. Anthracene-blue heated with zinc-fumes gives a white sublimate and a yellow amorphous substance. This product dissolves in acids, and exhibits a fine green

fluorescence very similar to that shown by acridine. It is a base of either the formula $C_{17}H_{11}N$ or $C_{17}H_{13}N$. The sulphate crystallises in fine yellow needles. This base has already been fully described by Graebe; but the vapour-density given by that chemist agrees nearly as well with the formula $C_{17}H_{11}N$ as with $C_{17}H_{13}N$, approximating however, more nearly to the value required by the latter.

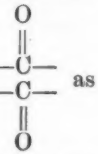
The calcium and barium salts of the alizarin-blue were obtained by neutralising an alkaline solution of the blue with calcium or barium chloride. They form greenish-blue amorphous precipitates, which are insoluble in water. Remarkable for its resistance is the copper salt, which is obtained by dissolving the blue in sulphuric acid, and pouring this solution into a diluted solution of copper sulphate. The copper salt of the blue separates directly in fine blue flocks, which in drying acquire a metallic lustre similar to that of Prussian blue. This salt, as its mode of formation shows, resists the action both of acids and of alkalis. It may be boiled with potash-lye, glacial acetic acid, or sulphuric acid, without being decomposed. Nitric acid, however, decomposes it when heated to about 90°, and the copper may thus be analytically determined. Yarn mordanted with the copper salt does not, however, give good shades.

Diacetylanthracene-blue.—This compound is easily obtained by heating the blue with acetic anhydride to 180°. It is very unstable, and on recrystallising it from glacial acetic acid or from alcohol, it is partly decomposed. When air-dried, it forms orange-coloured shining needles, which lose their lustre at 100°, and melt at 224·5°. Under certain circumstances it seems to crystallise with 1 mol. of acetic acid. On one occasion I obtained a compound which, when dried over sulphuric acid, formed small orange-coloured crystals melting at 196°, and giving figures nearly agreeing with those required by diacetylacetate. Acetyl chloride did not give good results.

The results above given are not sufficient to decide the nature of the alizarin-blue, the following formula, however, gives some account of the properties of this interesting body.



According to this formula, alizarin-blue should be nearly related to the aldehydines discovered by Ladenburg, which are formed when

aromatic orthodiamides act upon aldehydes. Now in mononitroalizarin the NO_2 group is in the ortho-position to the linking group  as shown by formation of purpurin from amidoalizarin ; and it is therefore very likely that a body having the character of an aldehydine may be formed. The formation of the alizarin-blue may, therefore, be explained as follows, thus :—The mononitroalizarin, when treated with sulphuric acid, gives monoamidoalizarin. (Perkin calls it purpuramide, *Chem. Soc. J.*, **30**, 578) ; glycerin, if treated with sulphuric acid, gives acroleïn ; and these two bodies unite in the nascent state to form alizarin-blue :

$$C_{14}H_9NO_4 + C_3H_4O = C_{17}H_{11}NO_4 + H_2O.$$

Numerous experiments, however, with amidoalizarin and acroleïn, or with a mixture of glycerin and sulphuric acid, have not given good results, the blue being formed only in traces in whatever way the mode of experimenting was varied.

That the substituting group is contained in the same benzene-nucleus that contains the two alizarin-hydroxyls is proved by the formation of phthalic acid, and that the substitution does not take place with the hydroxyls, is shown by the formation of a diacetyl-compound and of different salts. The green solution, which is obtained when alizarin-blue is dissolved in a small quantity of caustic potash, is very likely the acid salt, whilst the blue precipitate which forms on further addition of alkali is the normal salt of the alizarin-blue. If, therefore, both the hydroxyls are intact, only two cases can remain. Either the substitution takes place with the nitrogen or with the carbon combined with hydrogen. The first view seems to be the right one. If the amido-group were still intact, nitrous acid would form an azo-compound ; but instead of this, nitrous acid does not act upon the blue in the cold, and on heating it to boiling with alcohol, the nitrous acid converts it into phthalic acid. The formation of hydrocyanic acid by the action of melting potash on the salt which is obtained when the blue is treated with sulphuric acid, seems to support this view. Weselky and Benedikt, however (*Liebig's Annalen*, **196**, 340), found that when picric acid is boiled with caustic potash, and the melt acidulated with sulphuric acid, hydrocyanic acid is evolved. In the case of alizarin-blue, however, the existence of a nitro-compound is excluded. The great instability of the salts which alizarin-blue forms with acids seems also to show that the nitrogen in it is saturated.

LXXXIII.—*On Ethylene Chlorothiocyanate and its Oxidation into Chlorethylsulphonic Acid.*

By J. William James.

Maxwell Simpson, in 1863, showed that ethylene chloriodide, C_2H_4ClI, is formed by the action of iodine chloride, ClI, on ethyl iodide (*Ann. Chem.*, **125**, 121). L. Henry (*ibid.*, **156**, 12) subsequently obtained the chlorobromide, C_2H_4ClBr, by the action of free bromine on the chloriodide; and Lössner soon afterwards obtained the same compound by the action of antimony pentachloride, not in excess, on ethylene dibromide (*J. pr. Chem.*, **121**, 421). Compounds are also known in which one of the free combining units of ethylene is saturated by chlorine, and the other by a negative compound radicle, *e.g.*, *chlorethylsulphonic acid*, $C_2H_4Cl(SO_3H)$, and *ethylene monochlorhydrin*, $C_2H_4Cl(OH)$. Such compounds, however, have not hitherto been made directly from a haloïd compound of ethylene, but only by circuitous processes. It therefore seemed to me interesting to endeavour to replace the bromine in the compound, C_2H_4ClBr, by thiocyanogen (CNS), so as to form the new compound, *ethylene chlorothiocyanate*, $C_2H_4Cl(CNS)$, which would probably by oxidation give *chlorethylsulphonic acid*—

$$C_2H_4Cl(SO_3H),$$

identical or isomeric with that which Kolbe obtained in 1862 by acting upon sodium isethionate, $C_2H_4(OH)(SO_3Na)$, with phosphorus pentachloride, and decomposing the resulting chlorethylsulphonic chloride, $C_2H_4Cl.SO_2.Cl$, with water.

Preparation of Ethylene Chlorothiocyanate.

The chlorobromide of ethylene used to prepare the chlorothiocyanate was made by the method given by Lössner; that is, by acting upon ethylene dibromide with an equivalent quantity of antimony pentachloride, and *gently* warming, when the following reaction immediately takes place:—

$$2C_2H_4Br_2 + SbCl_5 = Br_2 + SbCl_3 + 2C_2H_4ClBr.$$

The mixture is then poured into a cylinder containing twice its volume of strong hydrochloric acid, when the ethylene chlorobromide settles at the bottom as a red, oily liquid—the trichloride of antimony and the greater portion of the bromine being held in solution by the hydrochloric acid. The oil is then separated by means of

a funnel provided with a stopper, again washed with hydrochloric acid, then with a *very weak* solution of sodium hydrate until white, and finally with water; after drying over calcium chloride the oil may be distilled, when the whole of the liquid will be found to pass over between 106° and 110°, and the portion boiling between 106—107° may be taken as pure. This is an excellent method for preparing this substance, owing to the great purity of the crude product, and the almost theoretical percentage which is invariably obtained.

To obtain the chlorothiocyanate of ethylene, 66 grams of potassium thiocyanate were weighed out and put into a common flask with about a one-fourth litre of 98 per cent. alcohol. The flask was then well shaken, and 100 grams of ethylene chlorobromide introduced. As no perceptible reaction took place, the flask was gently heated on a water-bath, and connected with a condenser, so arranged that the alcohol, after condensation, returned to the flask. Almost immediately the following reaction took place :—

$$C_2H_4ClBr + KCNS = C_2H_4Cl(CNS) + KBr.$$

The undissolved portion of the potassium thiocyanate rapidly disappeared, bromide of potassium taking its place, and after a few minutes' digestion, the reaction was complete, as was shown by testing with ferric chloride. The liquid was now filtered to get rid of the separated potassium bromide, and the alcohol evaporated as far as possible by the aid of a water-bath, after which the ethylene chlorothiocyanate remained behind as a disagreeably smelling oil. This oil contained an admixture of ethylene dithiocyanate, the formation of which was unavoidable. In other experiments a slight excess of the ethylene chlorobromide was used, but in spite of this the dithiocyanate formed. To obtain the ethylene chlorothiocyanate in the pure state, the product was treated as follows :—After having distilled off the alcohol, the remaining oil was put into a smaller retort, and distilled until the thermometer indicated 150° or thereabouts; the residue in the retort was now allowed to cool, and finally placed in a freezing mixture, by which means nearly the whole of the dithiocyanate of ethylene crystallised out. It is now only necessary to decant or filter off the oil, and distil in a suitable retort, the portion boiling between 202—203° being set aside for analysis. Care must be taken not to let the liquid distil after the thermometer shows about 210°, as a sudden decomposition then takes place, owing probably to the presence of a little dithiocyanate of ethylene. An analysis of the oil gave the following result :—

I. ·2148 gram burnt with copper oxide, lead chromate, and copper, gave ·0690 gram of water, and ·2325 gram carbonic anhydride.

III. ·3155 gram burnt in a stream of carbonic anhydride with

copper oxide and copper, gave 30·5 c.c. at a temperature of 7° C., and a pressure of 753 mm. of mercury.

II. ·2835 gram burnt with lime, gave ·3385 gram of silver chloride.

The above results calculated into percentages, gave numbers which agree with the formula $C_2H_4Cl(CNS)$.

	Calculated.		Found.		
			I.	II.	III.
C_3....	36	29·62	29·51	—	—
H_4....	4	3·29	3·53	—	—
Cl....	35·5	29·21	—	29·31	—
N	14	11·52	—	—	11·56
S	32	26·33	—	—	—
	121·5	99·97			

Ethylene chlorothiocyanate is a colourless oil having a most disagreeable smell, much resembling that of mustard oil. It is considerably heavier than water, in which it is insoluble. It is miscible with alcohol and ether. Its vapour, which burns with a violet flame, affects the eyes, making them water profusely, but does not cause sneezing like ethylene thiocyanate. Ethylene chlorothiocyanate boils between 202—203°, and at atemperature of —20° becomes syrupy, but does not solidify. It refracts light strongly.

Oxidation of Ethylene Chlorothiocyanate with Fuming Nitric Acid.

Twenty grams of the not quite pure oil were introduced into a small retort which was connected with a condenser; strong red nitric acid was then dropped in through a tap-funnel. The reaction takes place at once, and it is necessary to drop the acid in slowly, otherwise a most violent reaction occurs, causing effervescence and much loss of substance through imperfect condensation. After a time the reaction becomes sluggish, and the retort must be heated on a water-bath to complete the oxidation of the oil. A very convenient means of telling when the reaction is complete, is to take a few drops of the liquid out of the retort with a small pipette, and let them drop into a test-tube containing water; should the liquid dissolve in the water, no more chlorothiocyanate of ethylene is present. The addition of nitric acid should now be stopped, and the contents of the retort poured into a porcelain evaporating dish, which is then to be heated on the water-bath until the superfluous nitric acid is driven off, and acid vapours cease to be evolved. This operation takes some time, but it is absolutely necessary for the preparation of pure salts of the acid. The thick liquid remaining in the dish was found to react strongly acid. It was diluted with twice its volume of water, and divided into two

equal parts, one of which, to be described later on, was neutralised with silver carbonate, the other with barium carbonate. The excess of barium carbonate having been filtered off, the liquid was concentrated and placed under a desiccator. In a few hours a quantity of a salt crystallised out, which, as the following analysis shows, was the barium salt of the chlorethylsulphonic acid, which had not hitherto been obtained. The formula of this salt is $(C_2H_4ClSO_3)_2Ba + 2H_2O$. The salt was thoroughly dried by pressing and rubbing between filter-paper, and the results obtained were as follows:—

I. ·4167 gram of salt after drying at 100° lost ·0337 gram of water, and on heating with lime produced an amount of calcium chloride which yielded ·2590 gram of silver chloride.

II. ·1830 gram was ignited in a platinum crucible until all organic matter was decomposed, a drop or two of concentrated sulphuric acid added, and the whole evaporated to dryness, the residue being strongly heated; ·0920 gram of barium sulphate was obtained.

The results calculated into percentages, agree with the above-mentioned formula:—

	Calculated.		Found. I.	Found. II.
Ba	137	29·84	—	29·50
C_4	48	10·45	—	—
H_8	8	1·74	—	—
Cl_2	70	15·25	15·35	—
S_2	64	13·94	—	—
O_6	96	20·94	—	—
$2H_2O$	36	7·84	8·08	—
	459	100·00		

As only a small quantity of the salt was obtained, it was not recrystallised, and consequently the results are not quite so sharp as could be wished.

This salt crystallises in splendid star-like groups of needles; it is insoluble in alcohol and ether, and its aqueous solution may be boiled without suffering the least decomposition.

The part to be neutralised with carbonate of silver was introduced in small quantities at a time into a cylinder, darkened by being surrounded with black paper, and containing more than the quantity of silver carbonate required to neutralise the amount of acid. When all had been added, the excess of silver carbonate was filtered off, the liquid being screened from the light as much as possible: for it has already been shown by Kolbe that this salt is decomposed under the influence of light and heat. The clear filtrate was now evaporated in a vacuum,

light being as completely as possible excluded. After some days the salt crystallised out in indistinct crystals, and after drying between filter-paper was submitted to the action of ammonia in the following manner:—Four tubes of hard glass were prepared, sealed at one end, and into each ·5 gram of the silver salt was introduced, together with a slight excess of ammonia, which dissolved the salt. The tubes were now hermetically sealed and heated for 6—8 hours to 100—120°, when the following reaction took place:—$C_2H_4{<}^{Cl}_{SO_3Ag} + NH_3 = AgCl +$ $C_2H_4{<}^{NH_2}_{SO_3H}$ (taurine). On opening the tubes, there was, as expected, an inward pressure. In one of them the taurine had already crystallised in the characteristic monoclinic prisms, and on shaking the others it did so immediately. The contents of these tubes were now put into a beaker and heated with a little water on a water-bath until the excess of ammonia was completely expelled; by this procedure the taurine was dissolved, and the chloride of silver rendered insoluble. The latter was now filtered off, the filtrate concentrated, and the taurine allowed to crystallise. About ·7 gram of fairly pure taurine was obtained (= 70 per cent.), as the following results show:—

I. In ·1342 gram the nitrogen was determined by Will and Varentrapp's method, ·1048 gram of platinum being obtained.

II. ·0926 gram gave ·1730 gram barium sulphate, after fusion with potassium nitrate.

The above results agree closely with the percentage of nitrogen and sulphur in the formula $C_2H_4{<}^{NH_2}_{SO_3H}$.

	Calculated.	Found.
N	11·20	11·02
S	25·60	25·48

The taurine formed in this reaction agrees with that which is obtained from ox-bile, not only in its crystalline form, but likewise in its sparing solubility in water and insolubility in alcohol.

The following is a summary of the results described in the foregoing pages:—

1. By the action of potassium thiocyanate in equivalent quantity on ethylene chlorobromide, the bromine only becomes displaced, the electro-negative group, (CNS)′, taking its place, giving rise to ethylene chlorothiocyanate.

2. This compound, on oxidation with fuming nitric acid, forms chlorethylsulphonic acid, the group (CNS)′ having become oxidised into $(SO_2OH)'$.

3. By neutralising portions of this acid with the carbonates of barium and silver, the respective salts are formed.

4. By heating the silver salt with ammonia to 100—120° in sealed tubes, taurine is produced. Taurine has, therefore, been directly and easily made from ethylene gas according to the following reactions:—

1. $C_2H_4 + Br_2 = C_2H_4Br_2$.
2. $2C_2H_4Br_2 + SbCl_5 = Br_2 + SbCl_3 + 2C_2H_4ClBr$.
3. $C_2H_4ClBr + KCNS = C_2H_4Cl(CNS) + KBr$.
4. $C_2H_4Cl(CNS)$ on oxidation forms $C_2H_4<\begin{matrix}Cl\\SO_2OH\end{matrix}$.
5. $C_2H_4ClSO_3Ag + NH_3 = C_2H_4<\begin{matrix}NH_2\\SO_3H\end{matrix} + AgCl$.

The greater part of this research was performed in Leipzig under Professor Kolbe, and it was completed in the laboratory of the Bristol Mining School, where the action of other compound negative radicles on ethylene chlorobromide is being investigated.

LXXXIV.—*Notes on the Dissociation of Ammonia Iron Alum.*

By JOHN S. THOMSON.

WHILST engaged with some experiments, made with a view to eliminate the iron usually present in common alum, I was led to examine some of the conditions under which solutions of ferric salts decompose or dissociate; and in following out some of these experiments, it appeared that, in place of the tedious process of analysing each separate solution and precipitate, the same end might be arrived at by the use of standard solutions.

When a dilute neutral solution of a ferric salt is heated, it dissociates, and a basic salt is precipitated; now this basic salt is readily soluble in dilute sulphuric acid, and if the quantity of acid necessary to bring about the desired solution is known, an insight into the nature of the decomposition which has taken place can be arrived at. This end is readily obtained by the use of a standard solution of acid, and such was the process used throughout the following investigation.

Before proceeding to detail these experiments, it will be well to refer to the work already published in connection with this subject. Krecke (*J. pr. Chem.* [2], **3**, 286) confined himself to the study of the decomposition of solutions of ferric chloride. The chief results arrived at by this chemist were, that the more dilute the solution, the more readily did the decomposition take place, the phenomena

varying, however, with the temperature at which the experiment was made, and also with the length of time during which the experiment was continued. Wiedmann (*Ann. Phys. Chem.* [2], **5**, 45) made use of the magnetic properties of iron solutions to investigate the amount of dissociation which had taken place; but this method, although apparently capable of giving very accurate results, demands the use of expensive and complicated apparatus. The dissociation of solutions of ferric salts has also been made the subject of investigation by Tichborne (*Chem. News*, **24**, 209) and others. The chemist whose work, however, bears most immediately on the present subject is Naumann (*Deut. Chem. Ges. Ber.*, **8**, 1630; and **10**, 456). The salt, the dissociation of which he investigated, was potash-alumina alum, and in place of using acid for the purpose of redissolving the basic alt formed, he employed caustic alkali, a method which is of course quite inapplicable when dealing with ferric salts. He also, in a number of his experiments, operated with sealed tubes, in which he placed the alum without any solvent, thus introducing a number of other conditions beside the mere heating into the consideration of the dissociation of the salt.

The manner in which the experiments about to be detailed were carried out was as follows:—A certain quantity of the ferric salt to be experimented on was dissolved in a known quantity of water, and then boiled in a porcelain basin until the decomposition was complete, which usually was effected in the course of two or three minutes; very dilute standard acid was then slowly run in (the solution being kept boiling all the while) until the precipitated basic salt was redissolved, when the amount of acid which had been required was noted. By using white porcelain basins to effect the decomposition in, the point at which the precipitate is redissolved can be observed with great exactness. The strength of the standard sulphuric acid which was found to be most convenient was about one-third normal, that is to say, containing about 0·016 gram H_2SO_4 per c.c.

The ferric salt used throughout these experiments was ammonia iron alum, $Fe_2(NH_4)_24SO_4.24H_2O$, which was first analysed and found to be perfectly pure. A solution of this salt was prepared of such a strength that 20 c.c. contained a quantity of the alum equal to 0·1 gram Fe_2O_3, this strength of solution being found to keep perfectly for a very considerable period of time.

The first series of experiments was made with a view of ascertaining whether the dissociation increased regularly with the dilution of the solution, for which purpose iron alum equal to 0·1 gram Fe_2O_3, that is to say, 20 c.c. of the above solution was employed, the quantity of water added being regularly increased for each experiment; the results obtained are given in the following table:—

TABLE I.—*Ammonia Iron Alum* = 0·1 *gram* Fe_2O_3 *used in each case:*—

Fe_2O_3.	H_2O.	Standard acid in c.c. necessary for re-solution.*	Mean.	Difference.
0·1	50 c.c.	9·9; 9·55; 9·6	9·68 c.c.	—
„	60 „	10·6; 10·65	10·62 „	0·94 c.c.
„	70 „	11·7; 11·8; 11·7	11·73 „	1·11 „
„	80 „	12·8	12·8 „	1·07 „
„	90 „	14·0; 13·9	13·95 „	1·15 „

These experiments show that when a mean of all the results is taken, and the above quantity of iron alum is used, each addition of 10 c.c. of water requires an additional quantity of standard acid equal to 1·067 c.c., or 0·01753 gram H_2SO_4, to bring about re-solution.

The next series of experiments was made for the purpose of proving whether this quantity of acid increased regularly with an increase in the quantity of the iron salt.

TABLE II.—*Ammonia Iron Alum* = 0·15 *gram* Fe_2O_3 *used in each case:*—

Fe_2O_3.	H_2O.	Standard acid in c.c. necessary for re-solution.	Mean.	Difference.
0·15....	50 c.c.	10·5; 10·6; 10·4	10·5 c.c.	—
„	60 „	11·9; 11·9	11·9 „	1·4 c.c.
„	70 „	13·4; 13·5	13·4 „	1·5 „
„	80 „	14·95	14·95 „	1·55 „

Again taking the mean of these results, 1·483 c.c., or 0·02436 gram H_2SO_4, is arrived at, as the quantity of acid required to neutralise the dissociating effect of dilution of 10 c.c. of water, when iron alum equal to 0·15 gram Fe_2O_3 is employed. The quantity of acid required for this amount of iron alum, when calculated from the result given in Table I, is found to be 0·02629 gram, while that got by experiment is 0·02436 gram; this difference between the two figures, which corresponds to only 0·12 c.c. of standard acid, is not more than that which might have been expected from error of observation. Consequently it appears that the quantity of acid required to prevent dissociation increases regularly with the quantity of ferric salt present.

The non-correspondence of these figures with any possible theoretical reaction of the ferric salt, seemed to point out that the ammonia salt present in the ammonia iron alum had some influence on the reactions which took place, and in order to test this hypothesis a further series of experiments was started. These were conducted in

* The exact strength of the acid used in this and all the other series of experiments was 0·01643 gram H_2SO_4 per c.c.

a manner precisely similar to the former ones, the only difference being that sulphate of ammonia $(NH_4)_2SO_4$ equal to a given quantity of ammonia, $2NH_3$, was added in each case.

TABLE III.—*Ammonia Iron Alum* = 0·1 *gram* Fe_2O_3 *used in each case:—*

Fe_2O_3.	H_2O.	$2(NH_4)SO_4$ = $2(NH_3)$.	Standard acid in c.c. necessary for re-solution.	Mean.	Difference.
0·1....	60 c.c	0·05 gr.	13·7	13·7 c.c.	—
„	70 „	„	14·9; 14·8	14·85 „	1·15 c.c.
„	80 „	„	15·9	15·9 „	1·05 „

From these the quantity of additional acid required for each dilution of 10 c.c. of water is found to be 0·01807 gram H_2SO_4, which figure corresponds well with that found in Table I. By comparing the figure found in that table for 60 c.c. of water with that found in this for the same degree of dilution, and so also with those for 70 c.c. and 80 c.c., the amount of additional acid required for 0·05 gram ammonia (NH_3) in the form of sulphate is arrived at, and taking the mean of all the above experiments, the quantity is found to be 0·0509 gram H_2SO_4.

When iron alum equal to 0·15 gram Fe_2O_3 was used, the ammonia remaining the same, the following results were obtained:—

TABLE IV.—*Ammonia Iron Alum* = 0·15 *gram* Fe_2O_3 *used in each case:—*

Fe_2O_3.	H_2O.	$(NH_4)_2SO_4$ = $2(NH_3)$.	Standard acid in c.c. necessary for re-solution.	Mean.	Difference.
0·15 ..	60 c.c	0·05	14·9; 14·9	14·9 c.c.	—
„ ..	70 „	„	16·25; 16·4	16·37 „	1·47 c.c.
„ ..	80 „	„	17·9	17·9 „	1·53 „

giving as the quantity of extra acid required for each dilution of 10 c.c. of water, 0·02466 gram H_2SO_4, while for the ammonia the quantity is found to be 0·04937 gram H_2SO_4, which agrees well with that found when the smaller quantity of iron alum was employed.

Other experiments were made when the quantity of sulphate of ammonia used was raised so as to equal 0·10 gram NH_3, the iron alum used being respectively equal to 0·1 and 0·15 gram Fe_2O_3; when the smaller quantity was employed, the results found were that for each addition of 10 c.c. of water, the quantity of acid necessary to prevent precipitation was 0·0193 gram H_2SO_4, the quantity required for the ammonia salt in the same series being 0·0884 gram H_2SO_4. When the iron alum used was equal to 0·15 gram Fe_2O_3, the figures found

for the effects of the dilution with 10 c.c. of water and the above quantity of sulphate of ammonia were respectively 0·02505 gram and 0·08803 gram H_2SO_4.

Taking the mean of all the series of experiments, the quantity of sulphuric acid, H_2SO_4, required to prevent dissociation for each addition of 10 c.c. of water after 50 c.c., when ammonia iron alum equal to 0·1 gram Fe_2O_3 is used, is found to be 0·0186 gram, and when the iron alum is equal to 0·15 gram Fe_2O_3, the quantity is 0·02479 gram H_2SO_4, the other conditions remaining the same. The addition of sulphate of ammonia equal to 0·05 gram ammonia $(NH_3)_2$ to the ferric salt (whatever the quantity of iron alum employed), requires an additional quantity of sulphuric acid, equal 0·05005 gram, to counterbalance the effects of dissociation, and for sulphate of ammonia equal to 0·1 gram ammonia, the quantity of sulphuric acid is 0·08822 gram.

The very marked effect of sulphate of ammonia on the dissociation of ammonia iron alum led me to try whether sulphate of ammonia had the same effect when combined with another sulphate to form a double salt. The double salts experimented with were ammonia-alumina alum, $Al_2(NH_4)_24SO_4.24H_2O$; double sulphate of ammonia and magnesia, $Mg(NH_4)_22SO_4.6H_2O$; and double sulphate of ammonia and zinc, $Zn(NH_4)_22SO_4.6H_2O$, and in each of these cases the ammonia salt was found to have the same amount of influence as when uncombined.

In order to test whether potash salts could exercise a similar influence to those of ammonia, an amount of potash-alumina alum, $Al_2K_24(SO_4).24H_2O$, containing $(\frac{1}{2}K_2O)$ equivalent to the quantity of ammonia (NH_3) employed in former experiments, was added to the iron alum solution ; the amount of acid which was now required to dissolve the precipitate formed on boiling was found to be very much increased, seven or eight times that required when ammonia salts were used. This shows that the action of potash salts on ferric salts is much more energetic than that of ammonia salts. In order to be certain that the alumina present as sulphate in the potash alum employed exercised no influence on the dissociation, experiments were made with sulphate of alumina, but this salt was found to be without action on the ferric solution.

The experiments with simple dilution appearing to indicate that, if the solution of ammonia iron alum was sufficiently concentrated, no dissociation, or at least no precipitation, would take place on boiling, experiments were made to put this to the test, when it was found that in order to cause decomposition on boiling—

2 grams of ammonia iron alum		required	30·4 ; 29·1	c.c. of water.
3	,,	,,	,,	43 c.c. of water.
4	,,	,,	,,	57 ,,

the mean of these results showing that a solution of ammonia iron alum more concentrated than 1 gram in 14·37 c.c. of water, does not become dissociated on boiling.

The experiments detailed in the first part of this paper corroborate the results found by Krecke for ferric chloride, viz., the more dilute the solution, the more readily does dissociation take place; at the same time they prove that the dissociation increases regularly with the degree of dilution, this holding true even in the presence of other salts which act on the ferric solution.

The results given in Tables III and IV show that salts of ammonium have a very marked effect in increasing the dissociation of the ferric salt, this being the case even when they are in combination with other metallic salts to form double sulphates, &c. This effect also increases regularly with each increase in the quantity of the ammonium salt. Salts of the other alkalis were found to act in a similar manner, but were much more energetic in their action. As to the cause of this action of the alkali salts, it does not appear clear whether it is owing to the dissociation of the alkali salt itself, or merely to some sort of catalytic effect which they have on the ferric solution.

The results found when ammonia-alumina alum and sulphate of alumina were employed, appear at first sight to be somewhat at variance with those obtained by Naumann (*loc. cit.*); but from that chemist's investigations it would appear that alumina salts are dissociated only after prolonged heating, whereas in the present instance the heating was not continued for more than 10 minutes or so, this time being found sufficient to effect the complete dissociation of ferric salts, thus probably accounting for the negative results found with these salts. Naumann also worked chiefly with potash-alumina alum, whereas I employed the corresponding ammonia salt. Now in the case of iron salts, potash salts have a much greater effect on the dissociation than have those of ammonia; consequently, supposing that this applies equally in the case of alumina salts, it may also assist in accounting for the apparent discrepancy. The much more energetic action of salts of potash on ferric solutions, as compared with those of ammonia, is strikingly corroborative of the fact that potassium-iron alum is much less stable than the corresponding salt of ammonia.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1878–79.

November 7th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On the Red Colouring Matter of the *Lithospermum Erythrorhizon*:" by M. Kuhara.

Second Report to the Chemical Society on "Researches on some Points in Chemical Dynamics:" by C. R. Alder Wright and A. P. Luff.

"Note on the Constitution of the Olefines, produced by the action of Zinc upon Ethylic Iodide:" by E. Frankland and Leonard Dobbin.

"On the occurrence of Certain Nitrogen-acids amongst the Products of the Combustion of Coal gas and Hydrogen Flames:" by Lewin T. Wright.

"On the action of Bromine upon Sulphur:" (additional note) by J. B. Hannay.

"Researches in Dyeing," Part I. "Silk and Rosaniline:" by E. J. Mills and G. Thomson.

"Comparison of the actions of Hypochlorites and Hypobromites on some Nitrogen-Compounds:" by H. J. H. Fenton.

"Note on Two New Vegeto-Alkaloïds:" by Baron F. von Mueller and L. Rummel.

"On the Determination of Lithia by Phosphate of Soda:" by C. Rammelsberg.

November 21st, 1878.

R. Warington, Esq., in the Chair.

The following papers were read:—

"A Chemical Study of Vegetable Albinism:" by A. H. Church.

"Relation between the Melting Points of the Elements and their Coefficients of Expansion:" by T. Carnelley.

"Preliminary Notice on a Hydrate of Boron:" by F. Jones.

December 5th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

E. Waller, New York; Shigetake Sugiura, Hampstead Road; H. F. Cheshire, Hastings; J. Treharne, Leeds; H. J. H. Fenton, Christ's College, Cambridge; H. Green, Maidstone; J. Collins, Bolton-le-Moors; W. J. Noble, Keble College, Oxford; D. McAlpine, Edinburgh; A. E. Drinkwater, Chardstock; L. Green, Maidstone; Ringo Takemura, Japan; G. W. Slatter, Liverpool; P. H. Walsh, Manchester; J. J. Watts, Manchester; H. Eccles, Carnforth; E. W. Napper, Manchester; A. E. Arnold, Canonbury.

A paper was read by Dr. C. Meymott Tidy on the "Processes for Determining the Organic Purity of Potable Waters."

December 19th, 1878.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"Researches on the action of the Copper-Zinc Couple on Organic Bodies," Part IX. "Preparation of Zinc-methyl:" by J. H. Gladstone and Alfred Tribe.

"On the production of Oxides of Nitrogen by the Electric Arc in Air:" by T. Wills.

"The action of Alkaline-Hypobromite on Oxamide, Urea, and Potassium-Ferrocyanide:" by W. Foster.

"On two new Hydrocarbons obtained by the Action of Sodium on Turpentine Hydrochloride:" by E. Letts.

"On the Formation of Barium Periodate:" by S. Suguira and C. F. Cross.

"On Erbium and Yttrium:" by J. S. Humpidge and W. Burney.

January 16th, 1879.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On the Action of Isobutyric Anhydride on the Aromatic Aldehydes:" by W. H. Perkin.

"On two new Methods for the Estimation of Minute Quantities of Carbon: (I) Gravimetric, (II) Chromometric, and their Application to Water Analysis:" by A. Dupré and H. W. Hake.

"On Stannic Ethide:" by E. Frankland and A. Lawrance.

"On Aurin," (Part II): by R. S. Dale and C. Schorlemmer.

"The Derivatives of Diisobutyl:" by W. Carleton Williams.

"On the Action of Chlorine on Iodine:" by J. B. Hannay.

February 6th, 1879.

Dr. J. H. Gladstone, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

W. Stevenson, Montague Place, W.C.; F. R. Japp, Turnham Green; C. F. Cross, Brentford; H. Wilson, West Derby; C. E. Cassall, University College; A. E. Menke, Gower Street, W.C.; J. J. Broadbent, Brixton; E. A. Letts, Bristol; E. H. Rennie, Barnsbury, N.; S. Spencer, Southwark; C. W. Smith, Birmingham; A. J. G. Lowe, Croydon; T. Gough, Hammersmith; R. Gracey, Liverpool; P. P. Bedson, Marple, near Stockport.

The adjourned discussion on Dr. Tidy's paper on the "Processes for Determining the Organic Purity of Potable Waters" then took place.

February 20th, 1879.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On Colouring Matters derived from Diazo-compounds:" by Dr. Otto N. Witt.

"Investigations into the action of Substances in the Nascent and Occluded Conditions:" by J. H. Gladstone and Alfred Tribe.

"On some new Methods of Vapour-density Determination:" by J. T. Brown.

"On the Decomposition-products of Quinine, and the Allied Alkaloïds:" by J. J. Dobbie and W. Ramsay.

March 6th, 1879.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On the Quantitative Blowpipe Assay of Mercury:" by G. Attwood.

"On some Points in the Analysis of Combustible Gases, and in the Construction of Apparatus:" by J. W. Thomas.

"On the Action of Isomorphous Salts in exciting the Crystallisation of Supersaturated Solutions of each other, and some Experiments on Supersaturated Solution of Mixed Salts:" by J. M. Thomson.

"On Isomeric Dinaphthyls:" by Watson Smith.

March 20th, 1879.

Dr. J. H. Gladstone, President, in the Chair.

The following papers were read:—

"On Plumbic Tetrethide:" by E. Frankland and A. Lawrance.

"On the Decomposition of Water by Certain Metalloids:" by C. F. Cross and A. Higgin.

"On the Volumetric Determination of Chromium:" by W. J. Sell.

March 31st. (Anniversary Meeting.)

April 3rd, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"On a Gold Nugget from South America:" by Geo. Attwood.

"On Terpin and Terpinol:" by W. A. Tilden.

"On Lead Tetrachloride:" by W. W. Fisher.

"On the Transformation of Aurin into Trimethylpararosaniline:" by R. S. Dale and C. Schorlemmer.

"On the Solution of Aluminium Hydrate by Ammonia, and a Physical Isomeride of Alumina:" by C. F. Cross.

"Researches on Dyeing. Part II: Note on the Emission of Colouring Matter:" by E. J. Mills and Louis Campbell.

April 17th, 1879.

Dr. Roscoe, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

W. E. Blythe, Liverpool; W. A. Bradbury, Workington; A. H. Black, Glasgow; T. Griffiths, Birkenhead; W. T. Gent, Gainsborough; C. H. Hutchinson, Granville Park, S.E.; F. A. B. Jewson, Manchester Street, W.; W. Johnstone, Forest Hill; W. T. Lawson, Norwood; J. L. Macmillan, Chelsea; W. North, Bernard Street, W.C.; J. A. Ogilvie, Exeter; F. Podmore, Great Russell Street; W. Palmer, Reading; T. Palmer, Chiselhurst; G. Rait, Hampstead; W. Radford, Uxbridge; W. Stone, Bath; A. W. Stokes, Paddington, W.; W. Spottiswoode, Grosvenor Place; C. Slater, St. John's College, Cambridge; W. B. Turner, Leeds; T. L. Teed, Colebrook Row, N.; V. H. Veley, Chelmsford; T. Whitaker, Yorkshire; T. H. Walker, Carlisle.

The following papers were read:—

"On Heptane from *Pinus Sabiniana*:" by T. E. Thorpe.

"On the Determination of Tartaric Acid in Lees and Inferior Argols, with some Remarks on Filtration and Precipitation:" by Beaumont Grosjean.

"Conditions affecting the Equilibrium of certain Chemical Systems:" by M. M. P. Muir.

"On the action of Aqueous Hydrochloric Acid upon Bismuthous Oxide:" by M. M. P. Muir.

"On the action of Oxides on Salts." Part II: by E. J. Mills and J. W. Pratt.

"Examination of Substances by the Time Method:" by J. B. Hannay.

"Preliminary Note on certain Compounds of Naphthalene and Benzene with Antimony Trichloride, &c.:" by Watson Smith.

May 1st, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"On the Volumes of Liquids at their Boiling Points obtained from Unit-volumes of their Gases:" by W. Ramsay.

"On a Method of Precipitating Manganese entirely as Dioxide, and its Application to the Volumetric Determination of Manganese:" by J. Pattinson.

"On the Determination of Nitric Acid as Nitric Oxide by means of its Action on Mercury:" by R. Warington.

"On a New Class of Colouring Matters:" by Otto N. Witt.

May 15th, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"On Nitrification." Part II: by R. Warington.

"On the Alkaloïds of the Veratrums." Part II. "The Alkaloïds of *Veratrum album*:" by C. R. A. Wright and A. P. Luff.

"On the Alkaloïds of the Veratrums." Part III. "The Alkaloïds of *Veratrum viride*:" by C. R. A. Wright.

"On the Alkaloïds of the Aconites." Part IV. "The Alkaloïds of Japanese Aconite Roots:" by C. R. A. Wright and A. P. Luff (with Appendix by C. R. A. Wright and A. E. Menke).

"On the action of Hydrochloric Acid on Manganese Dioxide:" by S. U. Pickering.

"A Preliminary Note on some Reactions of the Ammonio-Chloride of Magnesium known as 'Magnesia Mixture:'" by H. D'Arcy Power.

"The Composition of Cows' Milk in Health and Disease:" by A. Wynter Blyth.

"Notes on the Effect of Alcohol on Saliva and on the Chemistry of Digestion:" by W. H. Watson.

June 5th, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"Contributions to the Theory of Fractional Distillation:" by T. E. Thorpe.

"Preliminary Note on the Action of Organo-Zinc Compounds on Quinones:" by F. R. Japp.

"Third Report to the Chemical Society on Researches on some Points in Chemical Dynamics." Section I: by C. R. A. Wright and A. P. Luff. Sections II, III, and IV: by C. R. A. Wright and E. H. Rennie.

"Theory of Fractional Distillation:" by F. D. Brown.

"On Chloro-stannic Acid:" by J. W. Mallet.

"On Indigo-purpurin and Indirubin:" by E. Schunck.

June 19th, 1879.

Dr. Roscoe, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

C. J. Wilson, Highbury; R. Reid, St. Paul's Road, N.W.; G. R. Tweedie, Brixton; W. T. Bayne, Devon; J. Fletcher, Dublin; H. Appleby, Lancashire; J. Sakurai, University College; A. E. Robinson, Birmingham.

The following papers were read:—

"On Gardenin:" by J. Stenhouse and C. E. Groves.

"On Dry Copper-Zinc Couples and Analogous Agents:" by J. H. Gladstone and Alfred Tribe.

"On the action of Sulphuric Acid on the Hydrocarbons of the Formula $C_{10}H_{16}$:" by H. E. Armstrong and W. A. Tilden.

"Researches on the Terpenes, Camphor and Allied Compounds," (Part I). "On Hydrocarbons associated with Terpenes and on the Formation of Cymene from Terpenes and Allied Compounds;" and (Part II), "On the Action of Iodine on Terpenes:" by H. E. Armstrong. (Part III). "On Camphor Derivatives:" by H. E. Armstrong and M. Matthews.

"Contributions to the History of Starch and its Transformations:" by H. T. Brown and J. Heron.

"On the Determination of Nitric Acid by means of Indigo, with Special Reference to Water Analysis:" by R. Warington.

"Notes on the Purple of the Ancients:" by E. Schunck.

"On the Heat of Formation of Aniline, Picoline, Toluidine, Pyridine," &c.: by W. Ramsay.

"On Ethylene Chorothiocyanate and its Oxidation into Ethylene-chlorosulphonic Acid:" by J. W. James.

"On the Boiling Points of Certain Metals and Metallic Salts:" by T. Carnelley and W. Carleton Williams.

Donations to the Library, 1878–79:—

"A Treatise on Chemistry." Vols. i and ii: by Professors Roscoe and Schorlemmer: from the Authors.

"A Manual of Practical Chemistry:" by A. Wynter Blyth: from the Publishers.

"A Manual of Inorganic Chemistry:" by C. W. Elliot and F. H. Storer: from the Publishers.

"Watts's Dictionary of Chemistry." Vol. iii. (Third Supplement). Part I: from Messrs. Longman and Co.

"An Introduction to the Study of Commercial Chemical Analysis:" by A. H. Allen: from the Author.

"Destructive Distillation:" by E. J. Mills, D.Sc., F.R.S.: from the Author.

"Food:" by A. H. Church: from the Author.

"Coal Mine-gases, and Ventilation:" by J. W. Thomas: from the Author.

"Cooley's Cyclopædia of Practical Receipts." by R. V. Tuson: from the Editor.

"Reports on the Exhibits connected with Materia Medica, Pharmacy, Chemical Industry, &c., in the Paris Exhibition, 1878:" from the Reporters.

"A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali:" by George Lunge. Vol. i: from the Author.

"Æneidea:" by James Henry: from the Trustees of the Author.

"Thermometric Scales:" from Thomas Twining, Esq.

"Le Calcul des Opérations Chimiques:" par B. C. Brodie, F.R.S.: from the Author.

"La Théorie Atomique:" par A. Wurtz: from the Author.

"Wärme und Elasticität:" von Dr. H. Scheffler: from the Author.

"Ausfürhliches Lehrbuch der Chemie:" von H. E. Roscoe und C. Schorlemmer. Zweiter Band, Erste Absheilung, Metalle: from the Authors.

"Die Chemische Synthese:" von Ad. Baeyer: from the Royal Bavarian Academy of Sciences.

Pamphlets:—

"The Mode of Combustion of the Blast-furnace:" by J. A. Church, Ohio: from the Author.

"Memoranda of Experiments conducted on the Farm and in the Laboratory of J. B. Lawes, F.R.S., at Rothamsted, Herts: from J. B. Lawes, Esq.

"Précis of the Report by Mr. Louis Schwendler on Experiments in Electric Lighting, carried on at the India Store Depôt:"
from Major-General Hyde, R.E.

"Is Higher Farming a Remedy for Lower Prices?" by J. B. Lawes, F.R.S.: from the Author.

"Analysis and Valuation of Fertilisers:" by A. R. Ledoux, Ph.D.:
from the Author.

"On Certain Products connected with Diabetes:" by E. W. Pavy, M.D., F.R.S.: from the Author.

"An Account of two Experiments illustrating the Effects of Starvation with and without Hard Labour, on the Elimination of Urea from the Body:" by William North, B.A.: from the Author.

"Remarks on the Sedimentary Formations of New South Wales:" by the Rev. W. B. Clarke: from the Author.

"The Heat of the Comstock Mines, Nevada:" by John E. Church:
from the Author.

"Gas in the House: some Hints and Suggestions:" by H. Faraday:
from the Author.

"The Sugar-beet of North Carolina:" by A. R. Ledoux, Ph.D.:
from the Author.

"Undeveloped Resources of Turkey in Asia:" by C. E. Austin:
from the Author.

"Sur la Production artificielle du Cornindon, du Rubis, et de différents Silicates crystallisés:" par MM. Frémy at Feil:
from the Author.

"Sur l'Ytterbine, terre nouvelle contenue dans la Gadolinite:" par C. Marignac: from the Author.

"Kurze Chemische Mittheilungen:" von F. Stolba:
from the Author.

"Beitrag zur Kenntniss einiger Gerbstoffbestimmungsmethoden:" von Franz Kathreiner: from the Author.

"Ur-Kemist-Tekniska Byröns:" verksamet af. A. Werner Cronquist: from the Author.

"Bränvinsstillverkningen i Sverge:" af. A. Werner Conquist och A. Seberg. 8vo. Stockholm, 1878.

Periodicals:—

"Philosophical Transactions for 1878:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh." Vol. xxviii, Part II (Session 1877–78).

"Proceedings of the same. Session 1877–1878:" from the Society.

"Report of the Forty-seventh Meeting of the British Association for the Advancement of Science, held at Plymouth in August, 1877:
from the British Association.

"Transactions of the Royal Irish Academy." Vol. xxvi, October, 1878: from the Academy.

"Transactions of the Cambridge Philosophical Society, 1879." Vol. xii, Part III.

"Proceedings of the same. Session 1878:" Vol. iii. Parts III and IV: from the Society.

"Leeds Philosophical and Literary Society; the Annual Report for 1877–78: from the Society.

"Proceedings of the Literary and Philosophical Society of Liverpool." Vol. xxiii (1877–78): from the Society.

"The Calendar of the Pharmaceutical Society of Great Britain, 1879:" from the Society.

"The Chemical News, 1878–79:" from the Editor.

"Journal of the Society of Arts, 1878–79:" from the Society.

"The Analyst for 1879:" from the Editors.

"The Chemist and Druggist, 1879:" from the Editor.

"Quarterly Journal of Science." Vol. ix: from the Editor.

"Quarterly Journal of the Geological Society:" from the Society.

"Annual Report of the South Australian Institute, 1877–78:" from the Institute.

"Journal of the Proceedings of the Royal Society of New South Wales, 1877." Vol. xi: from the Society.

"American Journal of Science and Arts." Vols. xvi and xvii: from the Editors.

"Journal of the Franklin Institute, 1879:" from the Institute.

"Proceedings of the American Chemical Society." Vol. i, Nos. 1—5; Vol. ii, Nos. 1—4: from the Society.

"The Princeton Review." May and July, 1878: from the Editor.

"Louisville Medical News." December, 1878: from the Publishers.

"Annual Report of the N. Carolina Experiment Station for 1879:" from the Reporter.

"Journal d'Hygiène." December, 1878: from the Publishers.

"Memorie dell' Accademia delle Scienze di Bologna." Serie 3. Tomo ix, Fasc. 3, 4; Tomo x, Fasc. 1, 2: from the Academy.

"Rendiconti della stessa Accademia." Anno 1878–79: from the Academy.

"Abhandlungen der Königlich-baeyrischen Akademie der Wissenschaften." XIII Band, 1 u. 2 Abtheilung: from the Academy.

"Sitzungsberichte der Königlich-baeyerischen Akademie der Wissenschaften." 1 Heft, 1878: from the Academy.

"Verhandlungen des Naturbistorisch-medicinishen Vereins zu Heidelberg," Neue Folge. II Band, 3 Heft: from the Society.

"Verhandlungen der Physikal-medicinishen Gesellschaft in Würzburg." XII Band, 1 u. 2 Heft, 1878: from the Society.

"Chemiker Zeitung, 1878–79:" from the Publishers.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1879.

A.

Armstrong, H. E., and W. A. Tilden, on the action of sulphuric acid on the hydrocarbons of the formula $C_{10}H_{16}$, 733.
Attwood, G., on a gold nugget from South America, 427.
—— quantitative assay of the ores and compounds of mercury by the blowpipe, 207.
Auerbach, G., alizarin-blue, 799.

B.

Baker, H., a study of certain cases of isomorphism, 760.
Baker, William, obituary notice of, 265.
Baker. See also Sugiura.
Bird, Alfred, obituary notice of, 266.
Blyth, A. W., the composition of cows' milk in health and disease, 530.
Brodie, B. C., on the decomposition of the simple weight χ effected by Victor Meyer, 673.
Brown, F. D., theory of fractional distillation, 547.
Brown, H. T., and J. Heron, contributions to the history of starch and its transformations, 596.
Burney. See Humpidge.

C.

Campbell. See Mills.
Carnelley, T., and W. C. Williams, on the boiling points of certain metals and metallic salts, 563.
Church, A. H., a chemical study of vegetable albinism, 33.
Cross, C. F., rehydration of metallic oxides, 796.
Cross, C. F., and A. Higgin, on the decomposition of water by certain metalloïds, 249.
Cross. See also Sugiura.

D.

Dale, R. S., and C. Schorlemmer, note on safranine, 682.
—— —— on aurin. Part II, 148.
—— —— suberic and azelaïc acids, 683.
—— —— transformation of aurin into trimethylpararosaniline, 562.
Dobbie, J. J., and W. Ramsay, on the decomposition-products of quinine and the allied alkaloïds. Second paper: oxidation of quinine, quinidine (conquinine), cinchonine, and cinchonidine, with permanganate, 189.
Dupré, A., and H. W. Hake, on two new methods for the estimation of minute quantities of carbon: (1) gravimetric, (2) chromometric, and their application to water analysis, 159.

F.

Fenton, H. J. H., comparison of the actions of hypochlorites and hypobromites on some nitrogen compounds, 12.
—— the action of phosgene on ammonia, 793.
Fisher, W. W., on lead tetrachloride, 282.
Foster, W., the action of alkaline hypobromite on oxamide, urea, and potassium ferrocyanide. Part II, 119.
Frankland, E. and A. Lawrence, on plumbic tetrethide, 244.
—— —— on stannic ethide, 130.

G.

Gladstone, J. H., and A. Tribe, investigations into the action of substances in the nascent and occluded conditions. Hydrogen (continued), 172.

Gladstone, J. H., and A. Tribe, on dry copper-zinc couples and analogous agents, 567.
—— —— researches on the action of the copper-zinc couple on organic bodies. Part IX. Preparation of zinc-methyl, 107.
Grosjean, B. J., on the determination of tartaric acid in lees and inferior argols, with some remarks on filtration and precipitation, 341.
Groves. See Stenhouse.

H.

Hake. See Dupré.
Hannay, J. B., examination of substances by the time method. Part I. Hydrates, 456.
—— on the action of bromine upon sulphur (additional note), 16.
—— on the action of chlorine upon iodine, 169.
Heron. See Brown.
Higgin. See Cross.
Humpidge, J. S., and W. Burney, on erbium and yttrium, 111.

J.

James, J. W., on ethylene chlorothiocyanate and its oxidation into chlorethylsulphonic acid, 806.
Japp, F. R., on the action of organozinc compounds on quinones (preliminary note), 526.
Johnson, G. S., on the occlusion of hydrogen by copper, 232.
Jones, F., on a hydride of boron (preliminary note), 41.

K.

Kuhara, M., contributions from the laboratory of the University of Tôkio, Japan:—(1) on the red colouring matter of the *Lithospermum erythrorhizon*, 22.

L.

Lawrence. See Frankland.
Luff. See Wright.
Lyttle, W. A., obituary notice of, 265.

M.

Malaguti, M., obituary notice of, 266.
Mallet, J. W., on chlor-stannic acid, 524.
Menke. See Wright.
Mills, E. J., and L. Campbell, researches in dyeing. Part II. Note on the emission of colouring matter, 290.
Mills, E. J., and J. W. Pratt, on the action of oxides on salts. Part II. 336.
Mills, E. J., and G. Thomson, researches in dyeing. Part I. Silk and rosaniline, 26.
Mueller, Baron F. von, and L. Rummel, note on two new vegeto-alkaloïds, 31.
Muir, M. M. P., contributions from the laboratory of Gonville and Caius College, Cambridge. No. 1. On the conditions affecting the equilibrium of certain chemical systems. No. 2. On the action of aqueous hydrochloric acid upon bismuthous chloride, 311.

N.

Nakamura, T., on a new method of determining sulphur in coal, 785.

O.

O'Sullivan, C., on the transformation-products of starch, 770.

P.

Pattinson, J., on a method of precipitating manganese entirely as dioxide, and its application to the volumetric determination of manganese, 365.
Perkin, W. H., on mauveine and allied colouring matters, 717.
—— on the action of isobutyric anhydride on the aromatic aldehydes, 136.
Pickering, S. U., on the action of hydrochloric acid on manganese dioxide, 654.
Pratt. See Mills.

R.

Rammelsberg, C., on the composition of lithia-micas, 19.

Rammelsberg, C., on the determination of lithia by phosphate of soda, 18.
Ramsay, W., on the heat of formation of aniline, picoline, toluidine, lutidine, pyridine, dipicoline, pyrrol, glycerol, and furfuraldehyde, 696.
—— on the volumes of liquids at their boiling points, obtainable from unit-volumes of their gases, 463.
Ramsay. See also Dobbie.
Rennie. See Wright.
Rummel. See Mueller.

S.

Schorlemmer. See Dale.
Schunck, E., notes on the purple of the ancients, 589.
—— on indigo-purpurin and indirubin, 528.
Sell, W. J., on the volumetric determination of chromium, 292.
Smith, A. J., the bromine derivatives of β-naphthol, 789.
Smith, Watson, preliminary note on certain compounds of naphthalene and benzene with antimony trichloride, &c., 309.
—— the isomeric dinaphthyls, 224.
Stenhouse, J., and C. E. Groves, on gardenin, 688.
Stewart, W. A., obituary notice of, 266.
Sugiura, S., and H. Baker, note on the magnesium vanadates, 715.
Sugiura, S., and C. F. Cross, on the formation of barium periodate, 118.

T.

Thomas, J. W., on some points in the analysis of combustible gases, and in the construction of apparatus, 213.
Thomson, J. M., on the action of isomorphous salts in exciting the crystallisation of supersaturated solutions of each other, and some experiments on supersaturated solutions of mixed salts, 196.
Thomson, J. S., notes on the dissociation of ammonia iron alum, 811.
Thorpe, T. E., a contribution to the theory of fractional distillation, 544.
—— on heptane from *Pinus sabiniana*, 296.
Tidy, C. M., the processes for determining the organic purity of potable waters, 46.
Tilden, W. A., on terpin and terpinol, 286.
Tilden. See also Armstrong.
Tribe. See Gladstone.

W.

Warington, R., on nitrification. Part II, 429.
—— on the determination of nitric acid as nitric oxide by means of its action on mercury, 375.
—— on the determination of nitric acid by means of indigo, with special reference to water analysis, 578.
Watson, W. H., notes on the effect of alcohol on saliva, and on the chemistry of digestion, 539.
Wiggin, John, obituary notice of, 265.
Williams, W. C., the derivatives of diisobutyl, 125.
Williams. See also Carnelley.
Wills, W. L., on the atomic weight of tellurium, 704.
Witt, O. N., on a new class of colouring matters, 356.
—— on colouring matters derived from diazo-compounds, 179.
Wright, C. R. A., the alkaloïds of the veratrums. Part III. The alkaloïds of *Veratrum viride*, 421.
Wright, C. R. A., and A. P. Luff, the alkaloïds of the aconites. Part IV. The alkaloïds of Japanese aconite roots, 387.
—— —— the alkaloïds of the veratrums. Part II. The alkaloïds of *Veratrum album*, 405.
—— —— third report to the Chemical Society on "Researches on some points in chemical dynamics." Section I, 475.
Wright, C. R. A., and A. E. Menke, Appendix to the alkaloïds of the aconites. Part IV. The alkaloïds of Japanese aconite roots, 399.
Wright, C. R. A., and E. H. Rennie, third report to the Chemical Society on "Researches on some points in chemical dynamics." Sections II, III, and IV, 475.
Wright, L. T, on the occurrence of certain nitrogen-acids amongst the products of combustion of coal-gas and hydrogen flames, 42.
Wurtz, Ad., on the constitution of matter in the gaseous state, 1.

INDEX OF SUBJECTS.

TRANSACTIONS. 1879.

A.

Abietene, 296.
Abstractors, instructions to, 276.
Acetylgardenic acid, 693.
Achroodextrin-γ, 778.
Achroodextrin-iii of Musculus and Gruber, 777.
Aconite roots, Japanese, alkaloïds of, 387.
—— —— non-crystalline alkaloïds of, 398.
Aconites, alkaloïds of, Part IV, alkaloïds of Japanese aconite roots, 387.
Air, estimation of carbonic acid and of volatile and suspended organic matter in, 168.
Albinism, vegetable, chemical study of, 33.
Albumin, estimation of, in milk, 531.
Alizarin-blue, 799.
—— —— action of bromine on, 803.
—— —— action of caustic potash on, 803.
—— —— action of chlorine on, 803.
—— —— action of sulphuric acid on, 803.
Alkaloïds, two new, 31.
Alstonine, 31.
Aluminium oxide, action of, on potassic carbonate, 336.
—— —— rehydration of, 798.
Amines, aromatic, progress of oxidation in mixtures of, 357.
Ammonia, action of phosgene on, 793.
—— aurin, 151.
Ammonium carbamate, action of hypochlorites or hypobromites on, 12.
—— fluosilicate, isomorphism of, with potassium fluoxyuranate, 762.
—— fluotitanate, isomorphism of, with potassium fluoxyuranate, 763.
—— fluoxyniobate, isomorphism of, with potassium fluoxyuranate, 762.
—— fluoxyuranate, crystalline form of, 767.
—— fluozirconate, isomorphism of, with potassium fluoxyuranate, 762.
—— iron alum, dissociation of, 811.
Aniline, heat of formation of, 696, 699.
—— pink, or safranine, 728.
—— and orthotoluidine sulphates, oxidation of a mixture of, 728.
—— and paratoluidine sulphates, oxidation of a mixture of, 728.
Anisoïl, β-parabutenyl-, 145.
Anniversary meeting, 257.
Anthracene-blue, 801.
—— —— diacetyl, 804.
Apparatus for gas analysis, 216.
Argol, inferior, determination of tartaric acid in, 341.
Aromatic aldehydes, action of isobutyric anhydride on, 136.
Atomic volume, 464.
Atomic weight of tellurium, 704.
Aurin, 148.
—— action of acetic chloride and acetic anhydride on, 153.
—— combinations of, with acids, 154.
—— tetrabrom-, 152.
—— transformation of, into triphenylpararosaniline, 562.
Azelaïc acid, 684.
—— —— dry distillation of, with lime, 687.
—— —— preparation of, 684.
Azobenzene, ebullition volume of, 472, 473.
—— sulphonic acid, metadioxy-, 183.
Azo colours, 189.

B.

Balance-sheet of the Chemical Society, 270.
—— —— of the Research Fund, 271.
Barium periodate, formation of, 118.
—— pimelate, 687.
Barley-extract, coagulation of, at different temperatures, 652.
Benzene, certain compounds of, with antimony trichloride, &c., 309.
—— specific volume of, 469.
Bismuthous oxide, action of aqueous hydrochloric acid on, 335.

Biuret, action of hypochlorites and hypobromites on, 14.
Boiling points of certain metals and metallic salts, 563.
Borneol (camphol) from colophene, 752, 755.
Boron hydride, 41.
Brass and zinc couple, 575.
Bromine, action of, on sulphur, 16.
Bromo-β-butenylbenzene, 139.
—— —— dibromide of, 139.
β-Butenylbenzene, 138.
—— bromo-, 139.
—— dibromide of, 139.
Butenylcinnamene, 141.
Butenylsalicyl hydride, 145.

C.

Calcium azelate, dry distillation of, 687.
—— pimelate, 686.
Camphene, action of nitric acid on, 757.
—— boiling point of, *foot note*, 744.
—— hydrochloride, inactive, melting point of, 744.
—— inactive, 743, 744.
—— oxidation of, 756.
—— pure inactive, preparation of, 759.
—— ("terebene") hydrochloride, action of alcoholic solution of potassium hydroxide on, 744.
Camphol (borneol) from colophene, 752, 755.
Camphor, inactive, action of nitric acid on, 757.
—— —— from inactive camphene, 756.
Camphoric acid from inactive camphor, 757.
Cane-sugar, action of normal malt-extract on, 609.
Carbon, a new gravimetric method for the estimation of minute quantities of, 159.
—— a new nephelometric method for the estimation of minute quantities of, 163.
—— estimation of, in certain metals, 168.
—— two new methods for the estimation of minute quantities of, and their application to water analysis, &c., 159.
—— and zinc couple, 575.
Carbonic acid and volatile and suspended organic matter in air, estimation of, 168.
—— anhydride, behaviour of hydrogenised copper in, 241.
—— oxide, behaviour of hydrogenised copper in, 242.
Caseïn, estimation of, in milk, 531.
Cevadic acid, 425.
Cevadine, 421.
Chemical dynamics, third report on researches on some points in, 475.
—— systems, conditions affecting the equilibrium of certain, 311.
Chlorethylsulphonic acid, oxidation of ethylene chlorothiocyanate into, 806, 808.
Chlorine, decomposition of, 678.
—— density of, at different temperatures, 676.
Chloroplumbate, 285.
Chlorstannic acid, 524.
Chromium oxide, rehydration of, 797.
Chromium, specific or ebullition volume of, 471.
—— volumetric determination of, 292.
Chromogen of *Purpura Lapillus*, 591.
—— —— colouring matter from, 594.
Chrysoïdine, 180.
Cinchonidine, oxidation of, with permanganate, 189.
Cinchonine, oxidation of, with permanganate, 189.
Coal-gas, occurrence of certain nitrogen acids amongst the products of combustion of, 42.
Coal, new method of determining sulphur in, 785.
—— oxidation of, by means of nitric acid and potassium chlorate, 785.
Cobalt sesquioxide, rehydration of, 796.
Colophene, 745.
—— behaviour of, on distillation, 748.
—— nature of, 733, 750.
—— distillate, examination of, 748, 751.
Colouring matter from the chromogen of *Purpura Lapillus*, 594.
—— —— emission of, 290.
—— —— red, of the *Lithospermum erythrorhizon*, 22.
—— —— allied to mauveine, 717.
—— —— a new class of, 356.
—— —— derived from diazo-compounds, 179.
Conquinine (quinidine), oxidation of, with permanganate, 189.
Copper, hydrogenised, behaviour of, in different gases, 240.
—— magnesium sulphate, examination of, by the time method, 461.
—— oxide, determination of relations existing between rate of reduction of by carbon oxide, time, and temperature, 502.
—— —— determination of relations existing between rate of reduction of by hydrogen, time, and temperature, 475.
—— —— experiments on the reduction

of by carbon oxide and hydrogen at comparatively low temperatures, in sealed tubes, 516.
Copper oxide, reduction of, in an atmosphere containing an excess of reducing agent, 521.
—— —— rehydration of, 798.
—— sulphate, examination of, by the time method, 460.
—— zinc couple, action of, on organic bodies. Part IX. Preparation of zinc-methyl, 107.
—— —— couples, dry, and analogous agents, 567.
—— —— sulphate, examination of, by the time method, 462.
Cork, oxidation of, 685.
Couple of compressed metals heated in hydrogen, 568.
—— of non-compressed metals heated in air, 569.
—— of non-compressed metals heated in hydrogen, 569.
Couples of various elements, 571.
Cows' milk, composition of, in health and disease, 530.
—— —— average composition of healthy, 535.
Cumenylcrotonic acid, 137.
Cuminic aldehyde, cumenylangelic acid, 136.
Cupric chloride, action of phosphorus on, 254.
Cupric oxide, reducing power of, 619.
—— —— and zinc couple, 577.
Cuprous oxide and zinc couple, 576.

D.

Dahlia, or ethylated mauveine, 721.
Decomposition of the simple weight χ effected by Victor Meyer, 673.
Dekamali gum, extraction of gardenin from, 688.
—— —— terpene from, 691.
α-Dextrin, 640, 772.
Dextrins, 771.
β-Dextrins, 774.
Dextrose, a product of the action of malt-extract on starch? 648.
Diacetylanthracene-blue, 804.
Diamidoazobenzene, 180.
Diastase, nature of, 650.
Diazo-compounds, colouring matters derived from, 179.
Diethyl-sulphone (sulphuric diethoxide), 245.
Digestion, chemistry of, 539.
Di-isobutyl, action of chlorine on, 126.
—— alcohols of, 127.
Di-isobutyl, derivatives of, 125.
—— iso-octoate, 129.
Di-isobutylketone, 130.
$\alpha\alpha$-Dinaphthyl, preparation of, 225.
$\beta\beta$-Dinaphthyl, preparation of, from a mixture of naphthalene and bromnaphthalene, 230.
Dinaphthyls, isomeric, 224.
—— —— determinations of the vapour-densities of, 226.
Dipicoline, heat of formation of, 696, 701.
Duboisine, 32.
Dyeing, researches in. Part I. Silk and rosaniline, 26.
—— researches on emission of colouring matter, 290.

E.

Ebullition-volumes, 468.
Erbium, 111.
Erythro-dextrin, 640.
Ethyl iodide, action of, on mauveine, 721.
—— iso-octoate, 129.
—— nitrate, ebullition-volume of, 472, 473.
Ethylmauveine, hydrochloride of, 723.
—— —— nitrate of, 724.
—— —— platinum salt of, 723.
—— —— platinum salt of, analysis of, 723.
Ethylsulphinic acid, barium salt of, 246.
Ethylsulphonic acid, 133.
—— —— chlor-, oxidation of ethylene chlorothiocyanate into, 806, 808.
Ethylated mauveine, 721.
Ethylene chlorothiocyanate, 806.
—— —— oxidation of, into chlorethylsulphonic acid, 806, 808.
Evaporating dish, suggested use of a metallic collapsive, in water analysis, 165.

F.

Faraday lecture, 1.
Ferric oxide, action of, on potassic carbonate, 337.
Ferro-manganese, determination of manganese in, 371.
Filtration, remarks on, 344.
Fractional distillation of substances which are not miscible one with the other, 549.
—— —— of substances which mix in

all proportions, and between which no combination of any kind is known to take place, 550.
Fractional distillation, theory of, 544, 547.
Furfuraldehyde, heat of formation of, 696, 702.

G.

Gadolinite, analyses of, 117.
Galactin, 532.
Gardenia lucida, terpene from, 691.
Gardenic acid, 691.
—— —— acetyl-, 693.
—— —— diacetyl-, 694.
Gardenin, 688.
—— acetyl derivatives of, 695.
—— action of nitric acid on, 691.
—— action of stannous chloride on, 695.
—— benzoyl derivatives of, 695.
—— extraction of, from Dekamali gum, 688.
Gas analysis, apparatus for, 216.
Gas, combustible, some points in the analysis of, and in the construction of apparatus, 213.
Glycerol, heat of formation of, 696, 702.
Gold nugget from South America, 427.
—— and zinc couple, 575.
Granulose, 610.
Guanidine carbonate, action of hypochlorites and hypobromites on, 14.
—— nitrate, action of hypochlorites and hypobromites on, 14.
—— sulphate, 794.
Gum, Dekamali, extraction of gardenin from, 688.

H.

Heat, action of, on malt extract, 606.
—— action of, on mauveine, 721.
—— action of, on telluric acid, 709.
—— amount of, evolved by the combustion of sulphur, 697.
—— of formation of aniline, picoline, toluidine, lutidine, pyridine, dipicoline, pyrrol, glycerol, and furfuraldehyde, 696.
Heptane from *Pinus Sabiniana*, 296.
—— —— optical activity of, 302.
—— —— refractive index of, 301.
—— —— specific gravity of, 299.
—— —— surface tension of, 305.
—— —— thermal expansion of, 300.
—— —— viscosity of, 302.
Hydrates, examination of, by the time method, 456.
Hydrocarbon, $C_{10}H_{20}$, 745.
Hydrocarbons of the formula $C_{10}H_{16}$, action of sulphuric acid on, 733.
Hydrogardenic acid, 694.
Hydrogen in the nascent and occluded conditions, action of, 172.
—— nascent, action of, on nitric acid, 172.
—— action of sulphuric acid on, 176.
—— occluded, action of, on nitric acid, 175.
—— action of, on sulphuric acid, 177.
—— occlusion of, by copper, 232.
—— occurrence of certain nitrogen acids amongst the products of combustion of, 42.
Hypobromites, actions of, on some nitrogen-compounds, 12.
Hypochlorites, actions of, on some nitrogen-compounds, 12.

I.

Indigo-purpurin, 528.
Indirubin, 528.
Induline, 188.
Iodine, action of chlorine on, 169.
—— reactions during the transformation of starch with malt-extract, 641.
Iron-magnesium sulphate, examination of, by the time method, 459.
—— oxide, rehydration of, 798.
Isobutyric anhydride, action of, on the aromatic aldehydes, 136.
Isomorphism, certain cases of, 760.
Iso-octoic acid and its salts, 128.
β-Isopropylbutenylbenzene, 141.
Isoterebenthene, so-called, 755.

J.

Japaconine, 393.
—— action of benzoic anhydride on, 396.
Japaconitine, 393.
—— action of benzoic anhydride on, 396.
—— action of concentrated tartaric acid solution on, 394.
—— action of saponifying agents on, 394.
Japanese aconite roots, alkaloïds of, 387.
—— —— —— non-crystalline alkaloïds of, 398.
Jervine, 407, 410, 416, 420, 421.
—— and its congeners, attempts to obtain derivatives of, 419.

L.

Lactochrome, 532.
Lacto-proteïn, estimation of, in milk, 532.
Lead, quantitative estimation of, 285.
—— chloride, action of chlorine on, 284.
—— tetrachloride, 282.
Lees, determination of tartaric acid in, 341.
Leucaurin, 150.
Liquids, volumes of, at their boiling point, obtainable from unit-volumes of their gases, 463.
Lithia, determination of, by sodium phosphate, 18.
—— micas, composition of, 19.
Lithospermum erythrorhizon, red colouring mattter of, 22.
Lutidine, heat of formation of, 696, 700.

M.

Magnesia alba, action of amorphous vanadic acid on, 714.
Magnesium-copper sulphate, examination of by the time method, 461.
—— iron sulphate, examination of, by the time method, 459.
—— zinc sulphate, examination of, by the time method, 457.
—— vanadates, 713.
—— and platinum couple, 576.
Malt-extract, action of heat on, 606.
—— action of, on bruised starch, 624.
—— action of, on maltose, 621.
—— action of, on starch, 621.
—— action of, on starch-paste, 626.
—— action of, on starch-paste at elevated temperatures, 630.
—— action of, on the transformed products of starch, 778.
—— normal, action of, on cane-sugar, 609.
—— influence of neutralisation on the action of, on starch, 642.
—— is dextrose a product of the action of, on starch? 648.
—— modification of the action of, on starch-paste by heat, 631.
—— previously heated, action of, on starch-paste, 629.
Maltose, 771.
—— action of dilute sulphuric acid on, 619.
—— action of malt-extract on, 621.
—— cupric oxide reducing power of, 619.
—— properties of, 618.
—— solution, density of, 618.
—— specific rotatory power of, 618.
Manganese, a method of precipitating, entirely as dioxide, and its application to the volumetric determination of, 365.
—— dichloride, solution of manganese dioxide in presence of, 669.
—— dioxide, action of dilute hydrochloric acid on, 666.
—— —— action of hydrochloric acid on, 654.
—— —— influence of temperature on the action of hydrochloric acid on, 670.
—— —— Nicklès' experiments on the action of hydrochloric acid on, 672.
—— —— secondary reactions of hydrochloric acid on, 665.
—— sesquichloride, attempts to obtain a double salt of, 671.
—— slags, &c., determination of manganese in, 372.
Manganiferous iron ores, determination of manganese in, 368.
Manganoso-manganic chloride, action of an excess of hydrochloric acid on, 668.
—— —— —— —— influence of temperature in the preparation of, 670.
—— —— —— —— table showing the effect of water on the stability of, 667.
Mass, influence of, in affecting the equilibrium of certain chemical systems, 313, 324.
Matter, constitution of, in the gaseous state, 1.
Mauveine acetate, 717.
—— acid hydrochloride of, 720.
—— action of acids on solutions of, 720.
—— action of ethyl iodide on, 721.
—— action of heat on, 721.
—— action of sulphuric acid on, 721.
—— analysis of the platinum salt of, 719.
—— and allied colouring matters, 717.
—— colouring matters allied to, 717.
—— ethylated, 721.
—— ethyl-, dichloride of, 723.
—— —— nitrate of, 724.
—— —— platinum salt of, preparation of, 723.
—— hydriodide, 721.
—— hydrochloride, analysis of, 718.
—— oxidation of, 728.
—— platinum salt of, action of water on, 720.
—— quantitative combination of, with hydrochloric acid, 719.
—— sulphate, 717.
Mercury, quantitative assay of the ores and compounds of, by the blowpipe, 207.
Metadiamidoazobenzene, hydrochloride of, 181.

Metadioxyazobenzene-sulphonic acid, 183.
Metallic oxides, rehydration of, 796.
—— salts, boiling points of certain, 563.
Metals, boiling points of certain, 563.
—— estimation of carbon in certain, 168.
Milk alkaloïds, isolation of, 531.
—— bitter principle in, 533.
—— cows', average composition of healthy, 535.
—— from diseased cows, composition of, 535—539.
—— quantitative estimation of the different constituents of, 534.
Molecular volume, 464.
Monobromophthalic anhydride, 792.
Monoxyazobenzene-sulphonic acid, sodium salt of, 184.

N.

Naphthalene, action of carbon bisulphide on, at a red heat, 229.
—— action of carbon tetrachloride on, at a red heat, 229.
—— action of chloroform on, at a red heat, 229.
—— certain compounds of, with antimony trichloride, &c., 309.
β-Naphthol, bromine-derivatives of, 789.
Naphthol, β-monobromo-, 789.
—— β-tetrabromo-, 791.
Nascent and occluded conditions, action of substances in the, 172.
Nicklès' experiments on the action of hydrochloric acid on manganese dioxide, 672.
Nitric acid, action of nascent hydrogen on, 172.
—— —— action of occluded hydrogen on, 175.
—— —— determination of, as nitric oxide by means of its action on mercury, 375.
—— —— determination of, by means of indigo, with special reference to water analysis, 578.
—— —— influence of chlorides in the determination of, as nitric oxide, by means of its action on mercury, 377.
—— —— influence of organic matter in the determination of, as nitric oxide, by means of its action on mercury, 379.
Nitrification, 429.
—— influence of cane-sugar on the process of, 434.
Nitrification, influence of light on the process of, 431, 449, 451.
—— influence of tartrates on the process of, 433.
—— influence of temperature on the process of, 436.
—— of nitrites, 452.
—— possibility of, without seeding, 452.
Nitrites, nitrification of, 452.
Nitrobenzene, ebullition-volume of, 472, 473.
Nitrogen-acids, occurrence of, amongst the products of combustion of coal-gas and hydrogen flames, 42.
—— compounds, action of hypochlorites and hypobromites on some, 12.
—— —— ebullition-volume of, 472.
—— behaviour of hydrogenised copper in, 242.
—— binoxide, density of, 677.
—— tetroxide, density of, at different temperatures, 676.

O.

Obituary notices, 265.
Ortho-butenylphenol, 142.
Orthotoluidine sulphate, action of potassic dichromate on, 728.
—— and aniline sulphates, oxidation of a mixture of, 728.
Oxamide, action of alkaline hypobromite on, 119.
Oxides, action of, on salts, 336.
—— metallic, rehydration of, 796.
Oxygen, specific or ebullition volumes of, 470.
Oxy-α-naphthyl, 184.
Oxy-β-naphthyl-azophenyl-sulphonic acid, sodium salt of, 184.

P.

Palladium and zinc couple, 575.
β-para-butenylanisoïl, 145.
Parabutenylphenol, 145.
Parasafranine and its salts, 729.
—— nitrate of, 730.
Paratoluidine sulphate, action of potassic dichromate on, 728.
—— and aniline sulphates, oxidation of a mixture of, 728.
Pattinson's method of determining manganese, 365.
Peonin or red corallin, 148.
Phenanthrene-quinone, acetyl-derivative of the action of zinc-ethyl on, 527.
—— —— action of zinc ethyl on, 526.

Phenol, ortho-butenyl-, 142.
—— parabutenyl-, 145.
Phenylamidoazobenzene, 185.
—— action of amylic nitrite and acetic acid on, 187.
Phenylangelic acid, 136.
Phenylcrotonic acid, 137.
Phosgene, action of, on ammonia, 793.
Picoline, heat of formation of, 696, 699.
α-Pimelic acid, aldehyde of, 686.
Platinum and magnesium-couple, 576.
—— and zinc-couple, 575.
Plumbic tetrethide, 244.
—— —— action of sulphurous anhydride on, 244.
Potable waters, processes for determining the organic purity of, 46.
Potassium chlorate, action of hydrogenised copper on, 240.
—— ferrocyanide, action of alkaline hypobromite on, Part II, 123.
—— fluoxyniobate, isomorphism of, with potassium fluoxyuranate, 761.
—— fluoxyuranate, monoclinic, analysis of, 767.
—— —— monoclinic, crystalline form of, 766.
—— —— monoclinic, preparation of, 763.
—— —— quadratic, analysis of, 764.
—— —— quadratic, crystalline form of, 763.
—— —— quadratic, preparation of, 763.
—— —— triclinic, analysis of, 766.
—— —— triclinic, crystalline form of, 764.
—— —— triclinic, preparation of, 763.
—— fluozirconate, isomorphism of, with potassium fluoxyuranate, 762.
—— and tellurium, bromide of, 711.
Precipitation, remarks on, of potassium bitartrate, 349.
Pseudojervine, 407, 413, 419, 421, 422.
Pseudo-mauveine, 726.
—— —— hydrochloride of, 726.
—— —— hydrochloride of, analysis of, 726.
—— —— platinum salt of, 727.
Punicin, 595.
Purple of the ancients, 589.
Purpura Lapillus, chromogen of, 591.
—— —— colouring matter from, 594.
Pyridine, heat of formation of, 696, 700.
—— series of bases, ebullition volume of, 472, 473.
Pyrrol, ebullition volume of, 472, 473.
—— heat of formation of, 696, 701.
Pytalin, 540.

Q.

Quinidine (conquinine), oxidation of, with permanganate, 189.
Quinine and the allied alkaloïds, decomposition-products of, 189.
—— oxidation of, with permanganate, 189.
Quinones, action of organo-zinc compounds on, 526.

R.

Red corallin or peonin, 148.
Red lead, action of hydrochloric acid on, 283.
Rosaurin, 159.
Rubijervine, 407, 412, 420, 422.

S.

Safranine, 682.
—— or aniline pink, 728.
—— para-, and its salts, 729.
—— —— nitrate of, 730.
Salicylic acid, use of, in arresting the transformation of starch, 630.
Saliva, action of, on a mixture of starch and alcohol, 541.
—— action of, on starch, 541.
—— effect of alcohol on, 539.
Salts, action of oxides on, 336.
—— anhydrous, rehydration of, 799.
—— isomorphous, action of, in exciting the crystallisation of supersaturated solutions of each other, 196.
—— metallic, boiling points of certain, 563.
—— mixed, experiments on supersaturated solutions of, 196.
Sesquistanethylic acetate, 135.
Silver pimelate, 686.
—— and zinc-couple, 574.
Sodium thio-tellurite, 705.
Solutions, supersaturated, action of isomorphous salts in exciting the crystallisation of each other, 196.
Specific volume, 464.
Spiegeleisen, determination of manganese in, 371.
Stannic ethide, 130.
—— —— action of sulphurous acid on, out of contact with air, 134.
—— —— action of sulphurous anhydride on, 131.
Stannic oxide, action of, on potassic carbonate, 338.

Stantriethylic acetate, 132.
— ethylsulphonate, 134.
— hydrate, 132.
— sulphate, 132.
Starch, action of malt-extract on, 621.
— action of malt-extract on, at different temperatures, 632.
— action of malt-extract on the transformed products of, 778.
— action of saliva on, 541.
— and its transformations, 596.
— influence of neutralisation on the action of malt-extract on, 642.
— iodine reactions during the transformation of, with malt-extract, 641.
— is dextrose a product of the action of malt-extract on? 648.
— modification of the action of malt-extract on, by heat, 631.
— molecular transformations of, 644.
— nature and properties of, 610.
— phenomena of the metastasis of, 622.
— soluble, 615, 772.
— soluble, action of potash on, 617.
— transformation-products of, 770.
— ungelatinised, action of malt-extract on, 621.
— use of salicylic acid in arresting the transformation of, 630.
Starch-cellulose, nature and properties of, 610.
Starch-dextrose, specific rotatory power of, 620.
Starch-paste, 613.
— — action of potash on, 616.
— — action of malt-extract on, 626.
— — action of malt-extract on, at elevated temperatures, 630.
— — action of previously heated malt-extract on, 629.
— — optical activity of, 616.
— — viscosity of, 614.
Steel, determination of manganese in, 372.
Suberic acid, 684.
— — dry distillation of, with lime, 687.
— — preparation of, 684.
Suberone, action of nitric acid on, 686.
— analysis of, 685.
— pure, preparation of, 685.
— vapour-density of, 686.
Substances, examination of, by the time method. Part I. Hydrates, 456.
Sulphur, amount of heat evolved by the combustion of, 697.
— in coal, new method of determining, 785.
— specific or ebullition volume of, 471.
Sulphuric acid, action of nascent hydrogen on, 176.
— — action of occluded hydrogen on, 177.
Sulphuric diethoxide (diethyl sulphone), 245.
Surface addition, influence of, in affecting the equilibrium of certain chemical systems, 319.

T.

Tartaric acid, determination of, in lees and inferior argol, 341.
Taurine, 810.
Telluric acid, action of heat on, 709.
Tellurium, atomic weight of, 704.
— conversion of tellurium dioxide into, 709.
— dioxide, 708, 711.
— — conversion of, into tellurium, 709.
— oxidation of, by aqua-regia, 710.
— oxidation of, with nitric acid, 708.
— pure, preparation of, 704.
— potassium bromide, 711.
Temperature, influence of, compared with that of mass in affecting the equilibrium of certain chemical systems, 331.
— — in affecting the equilibrium of certain chemical systems, 329.
Terebene, crude, examination of, 742.
— nature of, 733.
— preparation of, 734, 737.
— (camphene) hydrochloride, action of alcoholic solution of potassium hydroxide on, 744.
— hydrochloride, melting point of, 744.
Terpene from Dekamali gum (*Gardenia lucida*) 691.
Terpenes, 734.
— action of hydrochloric acid gas on, 754.
— action of sulphuric acid of various degrees of concentration on, 734.
— examination of the volatile optically inactive product of the action of concentrated sulphuric acid on, 742.
— examination of the volatile inactive product of the action of dilute sulphuric acid on, 747.
Terpilene, 745, 747, 754.
— dihydrochloride, 746, 747.
— monohydrochloride, 754.
— nature of, 733.
Terpin, 286.
Terpinol, 287.
— action of sulphuric acid on, 289.

Terpinol, dihydrochloride, 288.
Terpinols, natural, 289.
Tetrabromaurin, 152.
Time, influence of, in affecting the equilibrium of certain chemical systems, 316, 326.
Time method, examination of substances by. Part II. Hydrates, 456.
Toluidine, heat of formation of, 696, 700.
—— ortho-, and aniline sulphates, oxidation of a mixture of, 728.
—— para-, and aniline sulphates, oxidation of a mixture of, 728.
—— sulphate, ortho-, action of potassic dichromate on, 728.
—— sulphate, para-, action of potassic dichromate on, 728.
Toluylene blue, leuco-, compound of, 361.
—— —— reduction of, 360.
Tricarbopyridenic acid, 194.
Trimethylpararosaniline, transformation of aurin into, 562.
Triphenylrosaniline, 159.
Tropæoline O, 184.
—— OO, 187.
—— OOO, No. 1, 184.
—— OOO, No. 2, 184.
—— OOOO, 184.
—— Y, 184.
Turpentine, action of hydrochloric acid gas on, 754.
—— action of sulphuric acid on, 734.
—— examination of the volatile inactive product of the action of dilute sulphuric acid on, 747.

U.

Urea, action of alkaline hypobromite on, 122.

V.

Vegeto-alkaloïds, two new, 31.
Veratralbine, 415, 418, 420, 422, 424.
Veratria, 421, 424.
Veratroidia, 424.
Veratrum album, alkaloïds of, 405.
—— *viride*, alkaloïds of, 421.
Veratrums, alkaloïds of. Part II. Alkaloïds of *Veratrum album*, 405.
—— —— Part III. Alkaloïds of *Veratrum viride*, 421.

W.

Water, action of the halogens on, 255.
—— action of selenium, tellurium, and phosphorus on, 253.
—— action of sulphur on, 249.
—— analysis, special application of two new methods for the estimation of minute quantities of carbon to, 165.
—— —— suggested use of a metallic collapsive evaporating dish in, 165.
—— decomposition of, by certain metalloïds, 249.
Waters, potable, processes for determining the organic purity of, 46.
Weight χ, simple, decomposition of, effected by Victor Meyer, 673.

Y.

Yttrium, 111.

Z.

Zinc-ethyl, preparation of, by the copper-zinc couple, 571.
—— methiodide, 108.
—— methyl, preparation of, 107.
—— copper sulphate, examination of, by the time method, 462.
—— magnesium sulphate, examination of, by the time method, 457.
—— and brass couple, 575.
—— and carbon couple, 575.
—— and cupric oxide couple, 577.
—— and cuprous oxide couple, 576.
—— and gold couple, 575.
—— and palladium couple, 575.
—— and platinum couple, 575.
—— and silver couple, 574.

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ERRATA.

The asterisk in the second column indicates that the line is counted from the bottom.

Page.	Line.	Error.	Correction.
1	9	Ordinaire	Honoraire
3	28	important point	important point of my lecture
7	20	61°	65°
376	7	cap	cup
448	13	p. 376	p. 384
454	22	E3	E'3
562	13	Triphenylpararos-aniline	Trimethylpararosaniline
589	12*	Capillus	Lapillus
591	11*		
592	18*		
594	4 and 11		
677	3	1·02	1·92
,,	14	2·6°	2·6
,,	15	1·6°	1·6
685	25	Spiegal	Spiegel
,,	8*	products	product
,,	7	consist	consists
687	3	0·323	0·023
,,	14*	suberic	sebacic

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